U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-297 587

Wastewater Treatment in Coal Conversion

Water Purification Associates, Cambridge, MA

Prepared for

Industrial Environmental Research Lab., Research Triangle Park, NC

Jun 79

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-79-133
June 1979

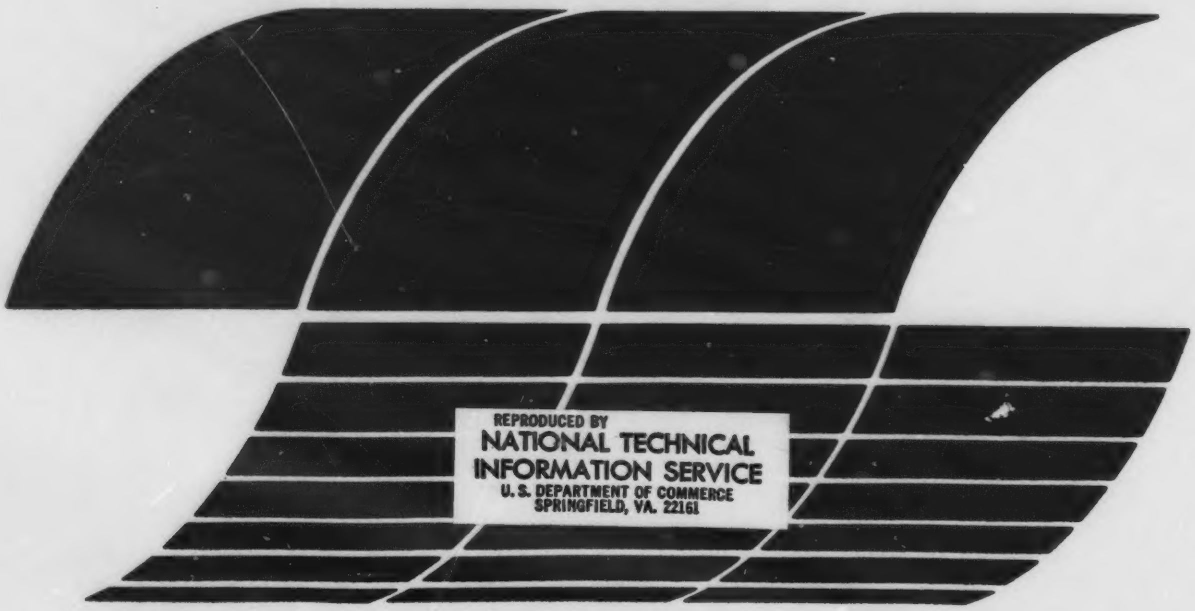
PB 297587

EPA

Wastewater Treatment in Coal Conversion

JUL 09 1979

Interagency Energy/Environment R&D Program Report



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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-79-133	2.	3. RECIPIENT'S ACCESSION NO. PB297587
4. TITLE AND SUBTITLE Wastewater Treatment in Coal Conversion		5. REPORT DATE June 1979
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R.E. Hicks, D.J. Goldstein, F.B. Seufert, and I.W. Wei		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Water Purification Associates 238 Main Street Cambridge, Massachusetts 02142		10. PROGRAM ELEMENT NO. EHE623A
		11. CONTRACT/GRANT NO. 68-03-2207
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 10/76 - 1/79
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is William J. Rhodes, Mail Drop 61, 919/541-2851.

16. ABSTRACT The report describes water treatment control technology specific to fuel conversion plant sites in the western U.S. Most plants converting coal to other fuels use a large quantity of clean water (as steam) and put out a large quantity of dirty water that is condensed when the products from the coal reactor are cooled. Treatment of this foul condensate is the subject of this report. The report discusses each aspect of water treatment separately. Procedures for removing phenolic compounds are discussed: they include distillation, extraction, and adsorption. The report includes design equations, step-by-step design procedures, and calculations for a typical unit. It also provides physical data that are required for design. The discussion of ammonia separation and recovery includes design equations and physical data. Illustrative calculations show how the design procedure is used. For biological treatment, the design procedures show how to destroy organic contamination (including phenol) in the condensate. It also discusses cooling tower control. An economical use of the foul condensate is treating it for makeup to a plant's cooling system. The report also reviews established procedures for sizing plant equipment.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Bioassay	Pollution Control	13B	06A
Coal Gasification	Cooling Towers	Stationary Sources	13H	13A,07A
Waste Water	Organic Compounds	Coal Conversion		
Water Treatment		Biological Treatment		
Phenols		Organic Contamination	07C	
Ammonia			07B	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 287
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE A13 - A01

EPA Form 2220-1 (9-73)

EPA-600/7-79-133
June 1979

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by

R.E. Hicks, D.J. Goldstein, F.B. Seufert, and I.W. Wei

Water Purification Associates
238 Main Street
Cambridge, Massachusetts 02142

Contract No. 68-03-2207
Program Element No. EHE623A

EPA Project Officer: William J. Rhodes

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

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ABSTRACT

Water Purification Associates has contracted with the U.S. Environmental Protection Agency to prepare a manual describing water treatment control technology specific to fuel conversion plant sites in the western United States. The information contained in this report may become part of an EPA Standards of Practice Manual.

Most plants converting coal to other fuels use a large quantity of clean water in the form of steam and put out a large quantity of dirty water that is condensed when the products from the coal reactor are cooled. The treatment of the foul condensate is the subject of this report.

Each aspect of water treatment is discussed separately in this report. The procedures for removing phenolic compounds are discussed in Section 3 and they include distillation, extraction and adsorption. We have included design equations, step by step design procedures, and the calculations for a typical unit. The physical data that are required for design also have been provided. Section 4 describing ammonia separation and recovery includes design equations together with the physical data. Illustrative calculations have been given to show how the design procedure is used. In Section 5, biological treatment, we have provided the design procedures showing how to destroy organic contamination including phenol in the condensate. Cooling tower control is the subject of Section 6. An economical use of the foul condensate is treating it for makeup to a plant's cooling system. Finally, Section 7 contains a review of established procedures for sizing plant equipment.

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CONVERSION OF AMERICAN TO INTERNATIONAL SYSTEM (SI)* UNITS

	To convert from	to	multiply by
LENGTH	ft	meters	0.305
AREA	ft^2	meters^2	0.0929
	acres	meters^2	4047
VOLUME	ft^3	meters^3	0.0283
	gallons	meters^3	0.00379
MASS	lb	kilograms	0.454
	tons	megagrams	0.907
WEIGHT RATE OF FLOW	10^3 lb/hr	kg/sec	0.126
	tons/day	kg/sec	0.0105
VOL. RATE OF FLOW	gallons/min	meters^3/sec	6.309×10^{-5}
	gallons/min	millimeters^3/sec	6309
	10^6 gallons/day	meters^3/sec	0.0438
ENERGY	Btu	kilojoule (= Newton x meter)	1.055
	kw-hrs	megajoules	3.60
POWER	H.P.	Joules/sec	746
	kw	Joules/sec	1000
	10^6 Btu/hr	kilojoules/sec	293
SPECIFIC ENERGY	Btu/lb	kilojoules/kg	2.324
PRESSURE	psia	kilopascall (= kilonewton/m^2)	6.895
WATER FOR ENERGY	gal/10^6 Btu	m^3/megajoule	3.592×10^{-6}
HEAT RATE	Btu/kw-hr	Joules/kw-sec	0.293
TEMPERATURE	^oF	^oK	$0.556\ (^oF + 459.7)$
HEAT TRANSFER COEFFICIENT	Btu/hr.ft^2.^oF	Joules/sec.m^2.^oK	5.674

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*Standard for Metric Practice, American Society for Testing and Materials, E380-76, 1976.

1. SUMMARY

Water Purification Associates has contracted with the U.S. Environmental Protection Agency to prepare a manual describing water treatment control technology specific to fuel conversion plant sites in the western United States. The information contained in this report may become part of an EPA Standards of Practice Manual.

Most plants converting coal to other fuels use a large quantity of clean water in the form of steam and put out a large quantity of dirty water that is condensed when the products from the coal reactor are cooled. The treatment of the foul condensate is the subject of this report. The condensate has contacted coal and crude gas and contains volatile products of coal pyrolisis and hydrogenation, principally phenols (mixed), other carbonaceous molecules and ammonia.

Each aspect of water treatment is discussed separately in this report. The procedures for removing phenolic compounds are discussed in Section 3 and they include distillation, extraction and adsorption. We have included design equations, step by step design procedures, and the calculations for a typical unit. The physical data that are required for design also have been provided. Section 4 describing ammonia separation and recovery includes design equations together with the physical data. Illustrative calculations have been given to show how the design procedure is used. In Section 5, biological treatment, we have provided the design procedures showing how to destroy organic contamination including phenol in the condensate. Cooling tower control is the subject of Section 6. An economical use of the foul condensate is treating it for makeup to a plant's cooling system. The level of treatment required and the effect on the cooling system of contaminated makeup are discussed. Finally, Section 7 contains a review of established procedures for sizing plant equipment.

2. INTRODUCTION

Water Purification Associates has contracted with the U.S. Environmental Protection Agency to prepare a manual describing water treatment control technology specific to fuel conversion plant sites in the western United States. The information contained in this report may become part of an EPA Standards of Practice Manual.

Most plants converting coal to other fuels use a large quantity of clean water in the form of steam and put out a large quantity of dirty water that is condensed when the products from the coal reactor are cooled. The condensed water contains coal decomposition products including mixed phenols and other organic compounds, ammonia, hydrogen sulfide and carbon dioxide. The treatment of the foul condensate is the subject of this report.

We have not included the treatment of source waters, whether they are reasonable quality surface or poor quality ground waters, because these methods follow standard design procedures that are not unique to fuel conversion plants.

The treatment of wastewaters other than the foul condensate also is not included; many are similar to those from coal fired power stations and not unique to fuel conversion plants. The condensate from a methanation reactor is clean enough to be reused as boiler makeup after a minor polishing. Domestic sewage can be treated adequately by conventional biological methods or commercial package units. How storm runoff is treated will depend on its source and the general cleanliness of the plant.

The selection of a process and the degree of treatment is influenced partly by the local discharge regulations, and the costs for energy and source water. The main factor, however, is the contaminants that are found in the wastewater and they are determined by the type of fuel and the fuel conversion process. Depending on the coal rank, condensate from gasification plants is generally cleaner the higher the temperature and the longer it remains in the gasifier. Nevertheless, all condensates contain varying degrees of ammonia, acid gases, organics (particularly phenols), suspended solids and oils.

To design any wastewater treatment an analysis of the condensate is needed. The analysis is not always straightforward because of the high concentrations of certain contaminants and the difficulty in preserving the water samples. We recommend a study of the techniques used by Luthy[1].

The first step in treating the condensate usually is the removal of solids and oils. Subsequent processing may follow the steps in Figure 2-1 or the sequence may be changed so that streams for reuse are taken after any step. For example, ammonia recovery alone may be sufficient treatment for water that is used in coal slurrying.

Each aspect of water treatment is discussed separately in this report. The procedures for removing phenolic compounds are discussed in Section 3 and they include distillation, extraction and adsorption. We have included design equations, step by step design procedures, and the calculations for a typical unit. The physical data that are required for design also have been provided.

Section 4 describing ammonia separation and recovery includes design equations together with the physical data. Illustrative calculations have been given to show how the design procedure is used.

In Section 5, biological treatment, we have provided the design procedures showing how to destroy organic contamination including phenol in the condensate. The section includes:

- air activated sludge process
- oxygen activated sludge process
- trickling filters
- anaerobic fermentation.

Cooling tower control is the subject of Section 6. An economical use of the foul condensate is treating it for makeup to a plant's cooling system. Using treated condensate has two advantages:

- The degree of treatment that is needed for cooling tower makeup is less than the treatment that would be needed to discharge into a waterway. (This statement is substantiated in Section 6).
- The use of source water can be kept to a minimum which is useful in the water-short western states where withdrawals are generally restricted.

Finally, Section 7 contains a review of established procedures for sizing plant equipment. Within each section we have used examples that best illustrate a particular design procedure. Because each section stands independently, the same example is not necessarily given in each section.

REFERENCE

1. Luthy, R.G., "Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters." Energy Research and Development Administration (now Department of Energy). Report FE-2496-8, 1977.

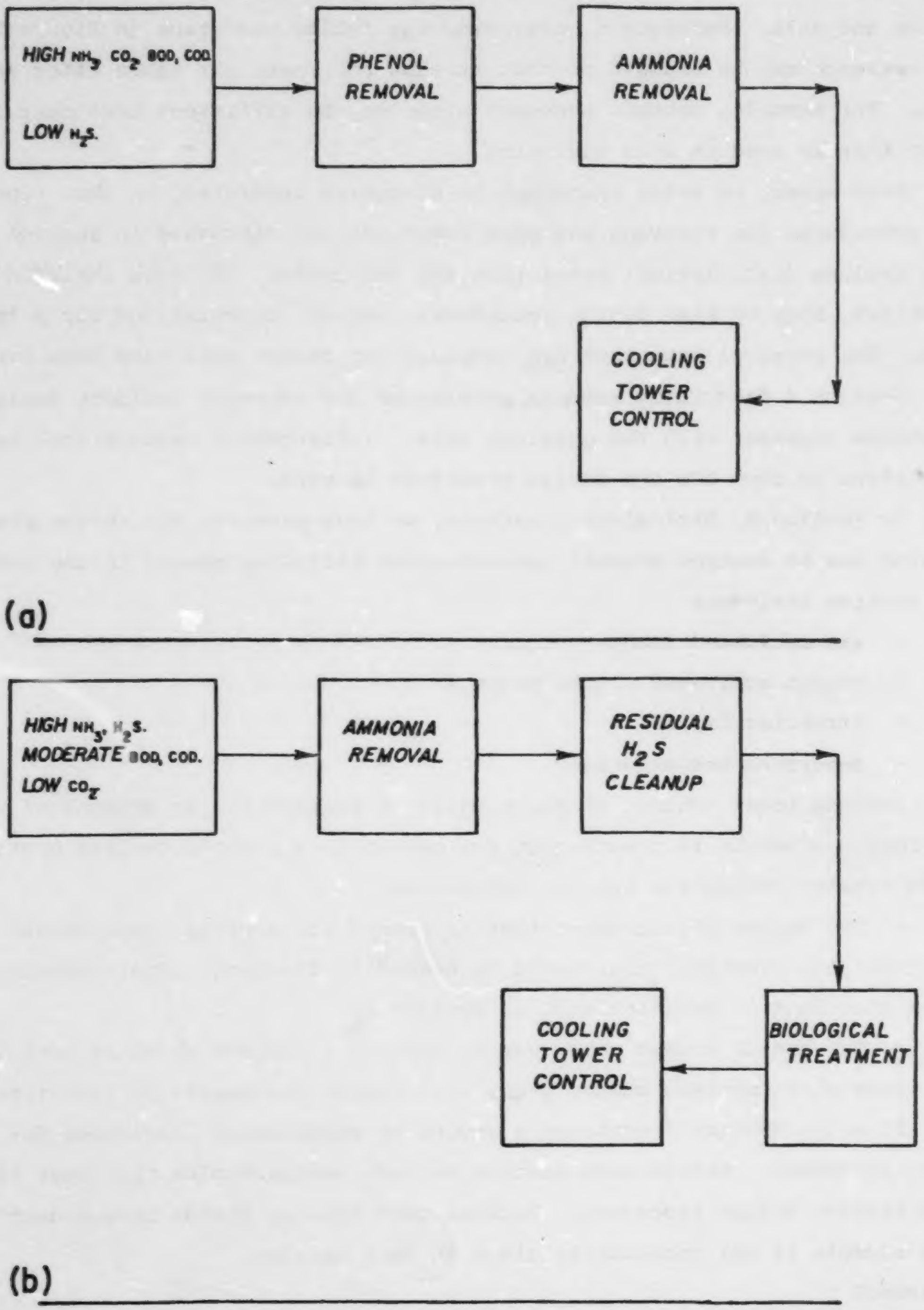

HIGH NH3, CO2 BOD, COD
LOW H2S.
PHENOL REMOVAL
AMMONIA REMOVAL
COOLING TOWER CONTROL
(a)
HIGH NH3, H2S.
MODERATE BOD, COD.
LOW CO2
AMMONIA REMOVAL
RESIDUAL H2 S CLEANUP
BIOLOGICAL TREATMENT
COOLING TOWER CONTROL
(b)

Figure 2.1. Simplified treatment schemes for treatment of fuel conversion plant wastewaters. (a) Phenolic process condensate; (b) High sulfur containing condensate but with medium to low concentrations of organics.

3. PHENOL REMOVAL PROCESSES

The wastewaters that are recovered from the quench and scrubbing units during coal conversion contain dissolved organic chemicals, acid gases and ammonia. The primary organic constituents are phenols including mono, di and trihydric members in proportions that depend on the type of gasifier and the temperature of the water/gas contact. One of the major water management problems in coal conversion processes is the lack of adequate quantitative data to facilitate the selection of an optimum phenol removal strategy[2]. Most experience to date in the removal of phenols has been in petroleum refining and coke oven plants.

An analysis of phenols that are found in the wastewaters from a Lurgi plant is shown in Table 3-1. The first high temperature quench produces the tar liquor with a 52% monohydric phenol content; the oily condensate is produced at a lower temperature and contains 89% monohydric phenols. Total phenol concentrations may vary from a negligible value in the relatively clean condensate from a Bigas gasifier, for example, to 8,000 mg/l in the wastewaters from a dissolving section of a Solvent Refined Coal (SRC) plant.

Phenols exert a biological oxygen demand of about 2.0 lb O_2/lb phenol, (the theoretical oxygen demand is 2.38 lb O_2/lb phenol), and must be removed before discharge. However, if the wastewater will be used as makeup to a cooling tower, probably up to 100 mg/l of phenol may remain (see Section 6).

The alternatives for treating phenol contaminated water generally fit one of the following processes[3]:

- Recovery (including distillation, solvent extraction, crystallization, activated carbon adsorption with solvent regeneration[3 to 10] and adsorption on synthetic polymers with solvent regeneration[11]) where the phenols are concentrated for reuse or sale,
- Degradation (including bio-oxidation, incineration, ozonation, contract disposal and activated carbon adsorption with thermal regeneration) with no attempt to recover the phenols,
- Recovery that is supplemented by degradation.

TABLE 3-1 ANALYSIS OF PHENOLS IN TAR LIQUOR AND OIL LIQUOR AT WESTFIELD WORKS[1]

	CONCENTRATION, mg/l	
	Tar Liquor	Oil Liquor
Phenols (total)	3,570	5,100
Monohydric Phenols	1,843	4,560
Phenol	1,260	3,100
O-Cresol	155	343
M-Cresol	170	422
P-Cresol	160	302
Total Xylenols	100	393
Other Phenols		
Catechol	555	190
3-Methyl	394	80
4-Methyl Catechol	385	110
3 : 5 Dimethyl Catechol	trace	trace
3 : 6 Dimethyl Catechol	45	trace
Resorcinol	272	176
5-Methyl Resorcinol	40	64
4-Methyl Resorcinol	36	--
2 : 4 Dimethyl Resorcinol	trace	trace
Monohydric Phenols as Percentage of Total Phenols	52%	89%

The economics of the processes depend on the total phenol load, lb/day, and the phenol concentration in the wastewater[12]. For example, because the cost of solvent extraction is independent of the influent concentration, this method becomes attractive as the influent concentration (or the amount of saleable byproduct) increases. Solvent extraction is capital intensive, however, and costs increase quickly when high phenol removal efficiencies are required. Thus, it is unlikely that solvent extraction would be used alone when the treated effluent will be discharged. Adsorption with solvent regeneration, using many special adsorbents[11], may be economical for the high efficiency removal of intermediate concentrations and useful as a backup to solvent extraction, or by itself.

Biological oxidation is economical when the influent concentration is below about 1,000 mg/l phenol and may be required to destroy organics that are left behind by extraction or adsorption. Ozonation and activated carbon adsorption with thermal regeneration are prohibitively expensive for all but the lowest concentrations and are unsuitable for fuel conversion wastewaters. Incineration and contract disposal are usually impractical.

A discussion of the recovery processes of distillation, solvent extraction and adsorption follows.

3.1 Phenol Removal by Distillation

There is an old process for the separation of phenol and water by distillation when no other components are present. Upon examination we find this process to be too expensive for use on process condensate and so we have not modified it to include the presence of ammonia and acid gases. However, the competitive process of solvent extraction and adsorption both require small units to separate phenol and water. The need for these small units will be made clear in the following sections. In this section a design procedure is given for the separation of water and phenol by distillation when no other components are present.

The phenol-water system forms an azeotrope at about 9.6% phenol by mass (98.01 mole %). Because wastewaters from coal conversion plants contain less than about 0.8% phenol, by a single step distillation we produce a virtually phenol-free bottoms, and an overhead approaching the azeotrope composition. The overhead consists of up to 10% of the feed and requires additional treatment to recover its water and phenol content. The recovery is done by cooling the azeotropic mixture which causes it to separate into a phenol rich and phenol lean fraction. The lean fraction is refluxed to the first distillation column, while the rich fraction is distilled to produce nearly pure phenol (Figure 3-1).

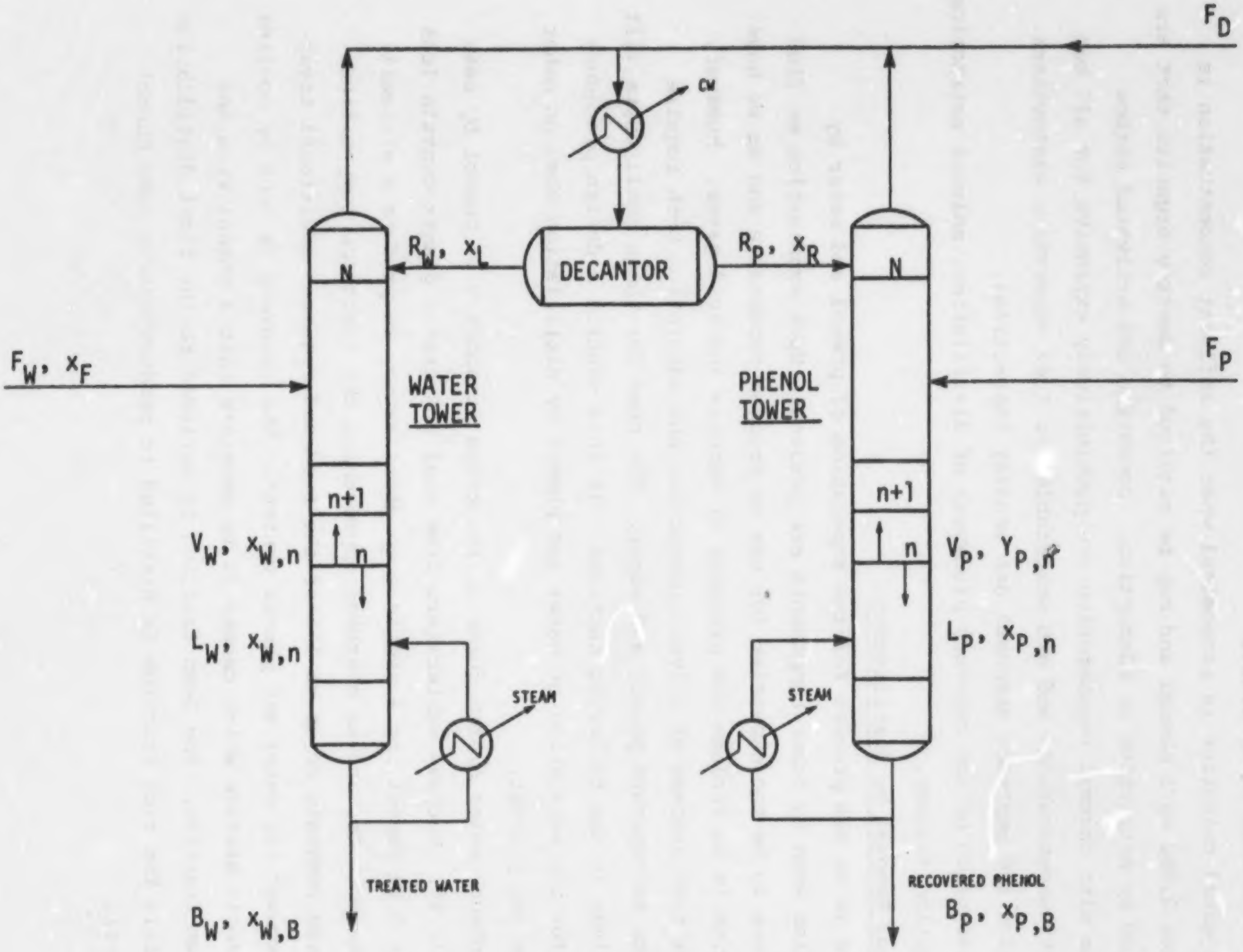

F_D
CW
R_W, x_L
DECANTOR
R_P, x_R
N
N
F_W, x_F
WATER TOWER
PHENOL TOWER
F_P
n+1
n+1
V_W, $x_{W,n}$
n
n
V_P, $Y_{P,n}$
L_W, $x_{W,n}$
L_P, $x_{P,n}$
STEAM
STEAM
TREATED WATER
RECOVERED PHENOL
B_W, $x_{W,B}$
B_P, $x_{P,B}$

Figure 3-1. Phenol removal and recovery by distillation.

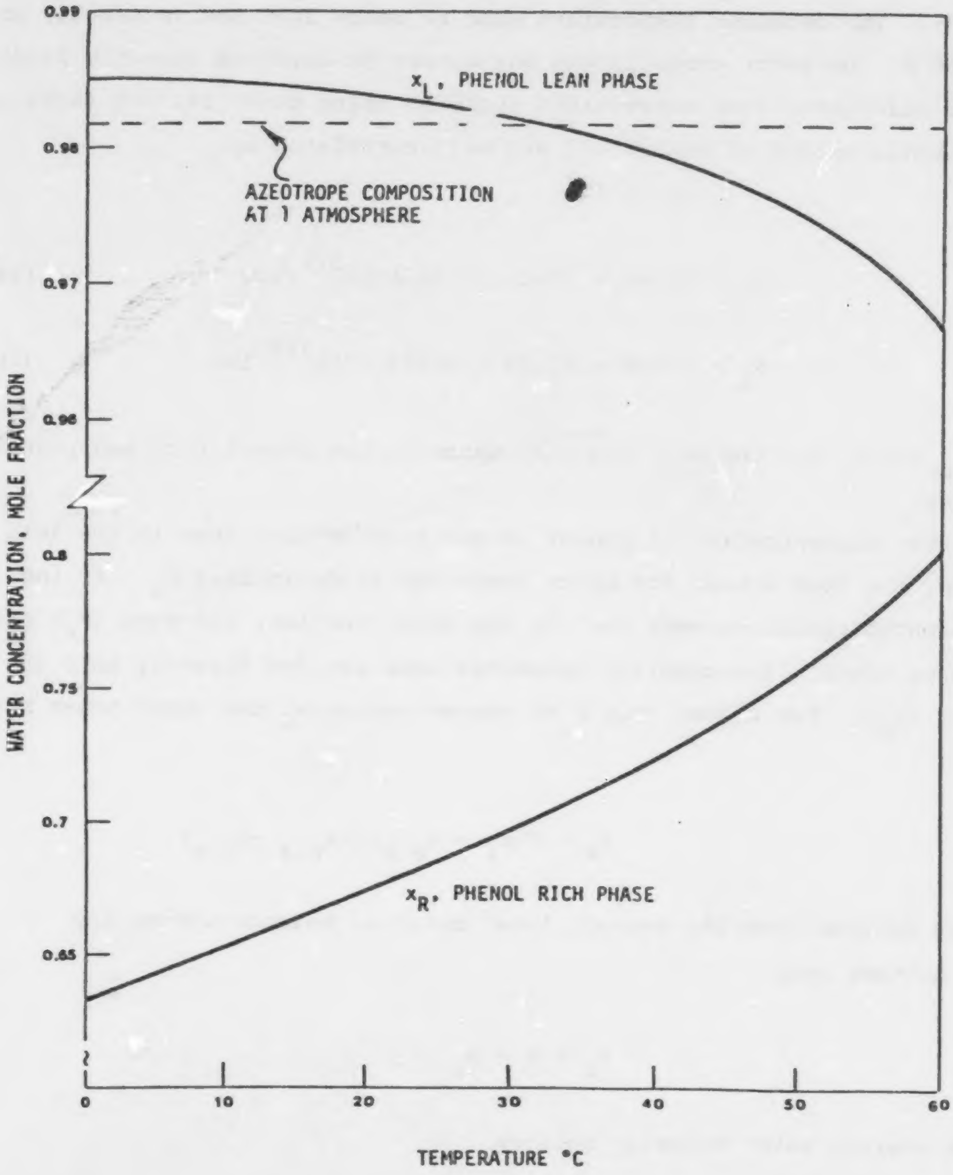


Figure 3-2. utual solubility of the phenol-water system at 1 atmosphere.

Design Procedure

The usual assumptions of constant molal overflow etc. are applicable and standard textbook methods may be used[24]. Feed composition, decantor temperature and the required bottoms composition for each tower are specified. The decantor temperature fixes the lean and rich phase compositions as shown in Figure 3-2. The decantor temperature must be below 34°C and is usually about 20°C = 68°F. Decantor compositions may either be obtained directly from the graph or calculated from expressions obtained using curve fitting techniques. The parabolic curves of Figure 3-2 are well correlated by:

$$x_R = 0.868 - (542 - 8.56.t°C)^{1/2}/100 \qquad (1a)$$

$$x_L = 0.976 + (0.90 - 0.019.t°C)^{1/2}/100 \qquad (1b)$$

where x_R and x_L are the mole fraction water in the phenol rich and phenol lean fractions.

If the concentration of phenol in the feed is less than in the lean fraction, the feed enters the water tower and is designated F_W. If the phenol concentration exceeds that in the rich fraction, the feed (F_P) enters the phenol tower. Intermediate concentrations are fed directly into the decantor (F_D). For a feed rate F at concentration x_f the water tower bottoms rate is:

$$B_W = F(x_f - x_{P,B})/(x_{W,B} - x_{P,B}) \qquad (2)$$

which is derived from the overall total material balance giving the phenol bottoms rate

$$B_P = F - B_W \qquad (3a)$$

and the overall water material balance

$$B_P \cdot x_{P,B} = F \cdot x_f - B_W \cdot x_{W,B} \qquad (3b)$$

The vapor (steam) rate V in each column must be sufficient to achieve the desired separation. If the vapor rate is too low, a "pinched" zone will develop either at the feed or top regions of the column. At the pinched condition the vapor leaving the region will be in equilibrium with the liquid entering that region. Applying this condition to the material balance for the region of interest leads to the following equations for the minimum vapor rate:

Water Tower

Pinch @ feed: $$V_{min} = B_P\,(x_{P,B} - x_f)/(y_f - x_f) \tag{4}$$

Pinch @ top: $$V_{min} = \left\{(F_D + F_P)(x_L - x_f) + B_P(x_{B,P} - x_L)\right\}/(y_L - x_L) \tag{5}$$

Phenol Tower

Pinch @ feed: $$V_{min} = B_W\,(x_{B,W} - x_f)/(y_f - x_f) \tag{6}$$

Pinch @ top: $$V_{min} = \left\{(F_D + F_W)(x_R - x_f) + B_W(x_{B,W} - x_R)\right\}/(y_R - x_R) \tag{7}$$

These equations are material balances. For example, Equation (4) follows from material balances taken from above the feed tray of the water tower and including the phenol tower, namely

$$V_{min} \cdot y_f = B_P \cdot x_{P,B} + L_W \cdot x_F$$

and

$$V_{min} = B_P + L_W$$

The limiting value for each tower is used to specify the actual vapor rate V for that tower. The vapor rate is related to the reflux rate R by

$$R = V + B - F \tag{8}$$

and is used to calculate the corresponding overhead vapor composition. For the water tower:

$$y_{W,N} = (F_W x_f + R_W x_L - B_W x_{B,W})/V_W \tag{9}$$

Enough information is now available for the tray calculations that are conveniently started at the bottom of each tower. Below the feed a material balance yields:

$$x_{n+1} = (Bx_B + Vy_n)/(R + F) \qquad (10)$$

The feed is introduced on the tray where the calculated x_n exceeds x_f. Above the feed a material balance yields:

$$x_{n+1} = (Bx_B + Vy_n - Fx_f)/R \qquad (11)$$

The equilibrium vapor composition y_n that is needed for each tray can be found using the method outlined below. The top tray is where the equilibrium vapor composition reaches the value given by Equation (9).

Phenol-water Vapor-liquid Equilibria

Published equilibrium data[18,29-32] for the phenol-water system were correlated according to the van Laar equations[27]:

$$\log Z_A = A/[1 + Ax_A/(Bx_B)]^2 \qquad (12)$$

and

$$\log Z_B = B/[1 + Bx_B/(Ax_A)]^2 \qquad (13)$$

where $$Z_A = y_A P/(p_A^* x_A), \; Z_B = y_B P/(p_B^* x_B) \qquad (14)$$

P = total system pressure,

p^* = vapor pressure

x_A = mole fraction water

x_B = mole fraction phenol

The coefficients A and B in the van Laar equations can be found using:

$$A = \log Z_A \, [1 + x_B \log Z_B/(x_A \log Z_A)]^2 \qquad (15)$$

and $$B = \log Z_B \, [1 + x_A \log Z_A/(x_B \log Z_B)]^2 \qquad (16)$$

These coefficients were estimated using azeotrope composition data (Figure 3-3). The resulting calculated vapor-liquid curves were compared with experimental data. In general the coefficients evaluated at the azeotrope did not adequately represent the data in the regions x → 1 and x → 0 because the calculated values of the coefficients are very sensitive to small errors in the azeotrope temperature and composition. After some adjustment it was found that the van Laar coefficients that best represent the data could be correlated by:

$$A\ (\text{water}) = 0.324 - 0.00052t°C \quad 55 < t°C < 240 \tag{17}$$

$$B\ (\text{phenol}) = 1.941 - 0.00352t°C \quad 55 < t°C < 240 \tag{18}$$

The equations give satisfact[illegible]urves over the full concentration range. Some calculated curves for the water distillation tower are shown in Figure 3-4 and for the phenol distillation tower in Figure 3-5.

A trial and error method is used to calculate vapor compositions using the Van Laar equations.([illegible]) To begin, a temperature is assumed and the corresponding water and phenol vapor pressures determined. Tabulated phenol vapor pressures were correlated by:

$$\log_{10} P^*_{\text{phenol}} = 7.495 - 1723.6/(192.3 + t°C) \tag{19}$$

The vapor pressure of water may be obtained from:

$$\log_{10} P^*_{H_2O} = 7.967 - 1668.2/(228 + t°C) \tag{20}$$

Equations (19) and (20) are for pressures in mm Hg. Knowing the vapor pressures, vapor compositions may be calculated using Equations (12) - (14). We then test whether

$$y_{H_2O} + y_{\text{phenol}} = 1.0 \tag{21}$$

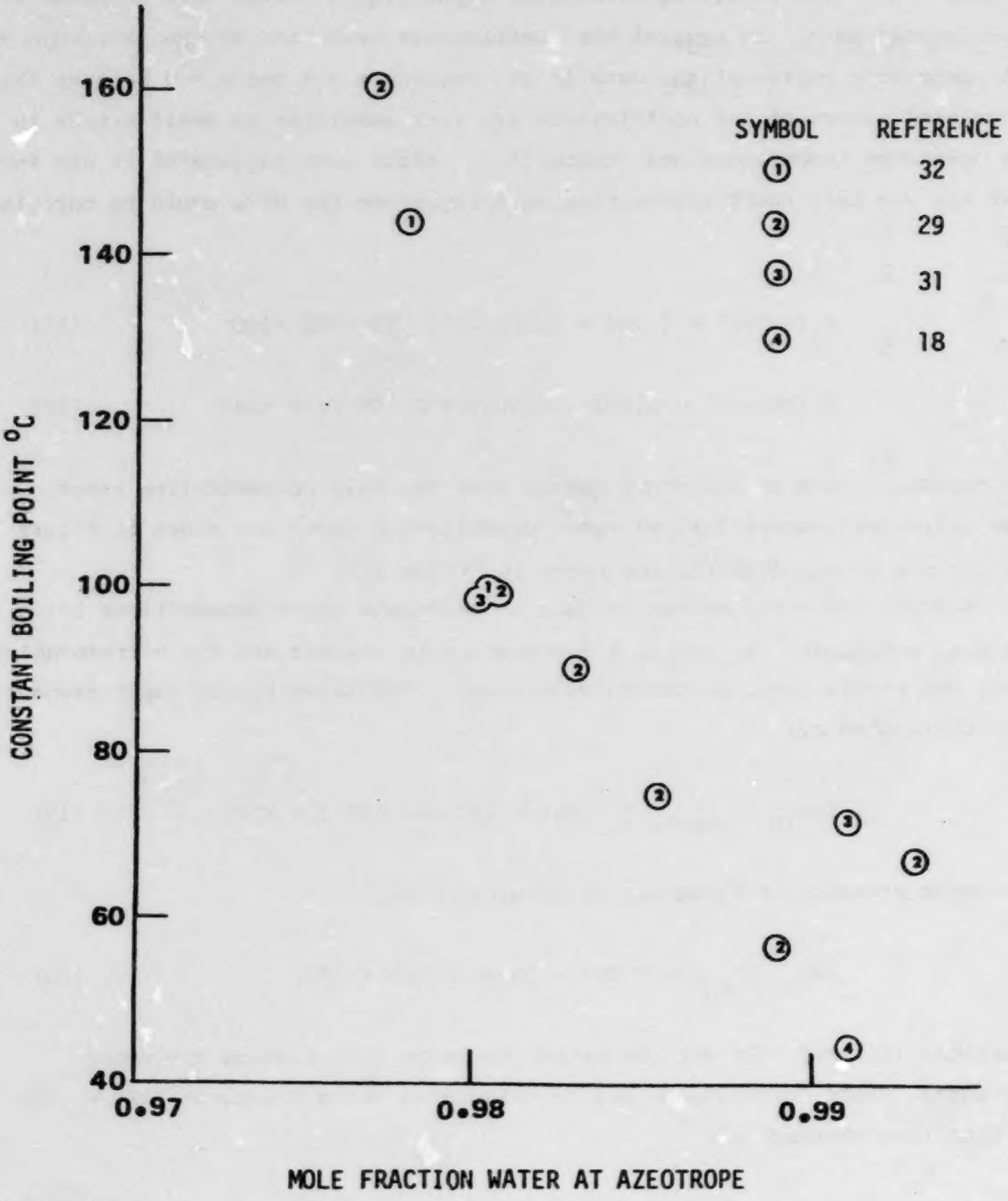


Figure 3-3. Azeotrope data for phenol-water system.

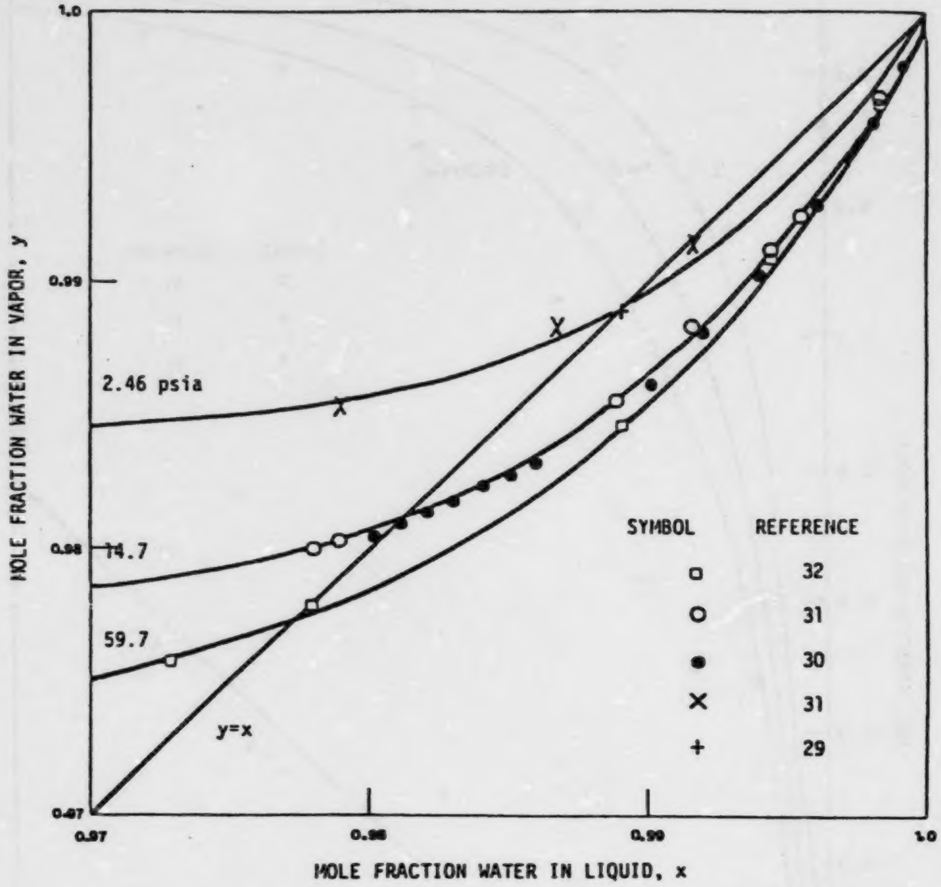


Figure 3-4. Phenol-water vapor-liquid data on water side of azeotrope. Curves calculated using van Laar equations with Equations (17) & (18).

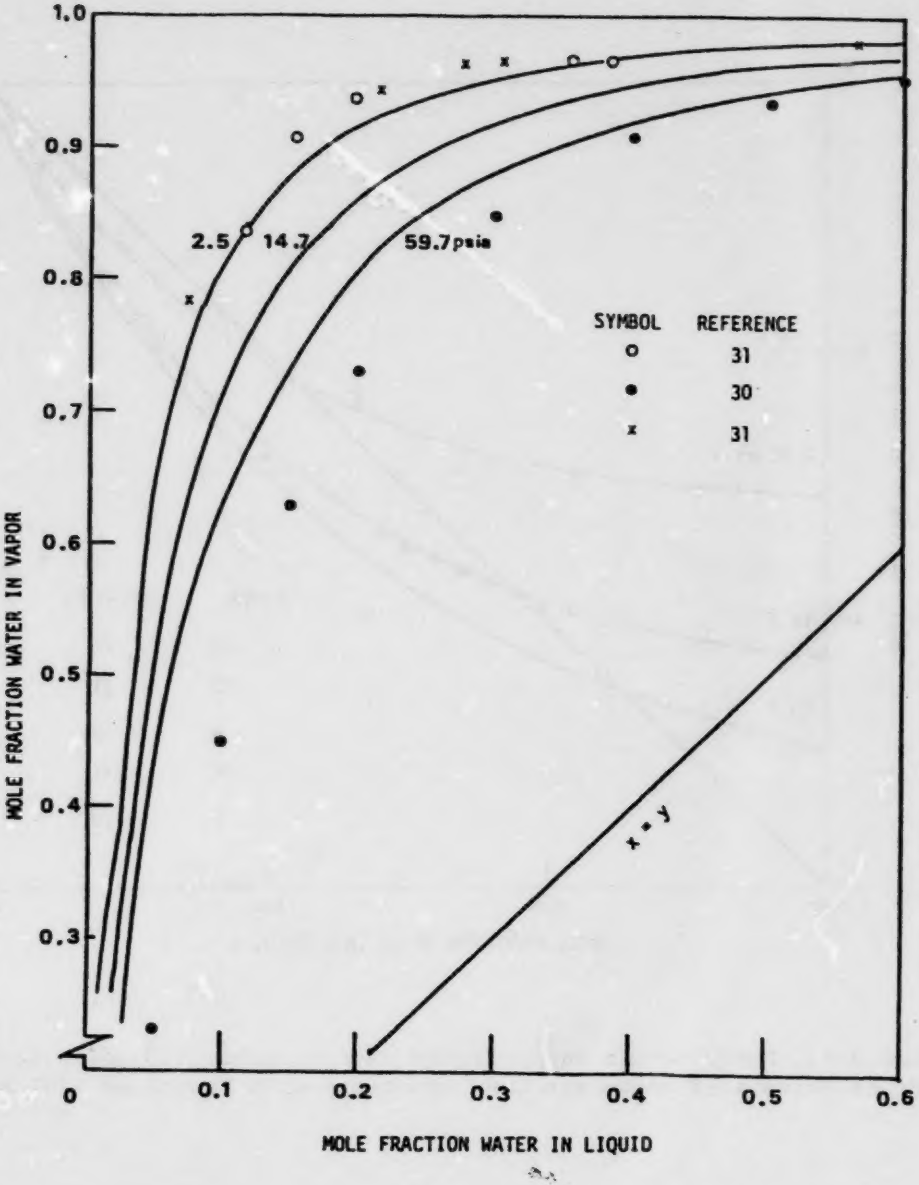


Figure 3-5. Phenol-water vapor-liquid data on phenol side of azeotrope. Curves calculated using van Laar equations with Equations (17) & (18).

If not, a new temperature is selected and the process is repeated until Equation (21) is satisfied.

3.1.1 Example: Design of Phenol Distillation System

To check our equations the phenol distillation example used in Reference 24 was selected. The feed contains 1 mole % phenol (52,200 ppm) and will be split into a 99.99% pure phenol stream and a 99.999% pure water stream. The decantor is cooled to 68°F and the reflux streams are heated to their equilibrium temperatures before they enter the columns.

(a) Stream Specification. We express concentrations as mole fraction water: $x_f = 0.99$, $x_{W,B} = 0.99999$, $x_{P,B} = 0.0001$. The feed composition falls on the water side of the azeotrope so $F_W = 100$, $F_D = F_P = 0$. The pressure at the top of the columns is taken to be 15 psia.

(b) Decantor Streams. Using $t_D = 68°F$ (20°C) the compositions of the lean and rich reflux streams are calculated from:

Eq. (1a): $x_R = 0.6754$

Eq. (1b): $x_L = 0.9835$

(c) Bottoms Split. Equation (2) is used to calculate the bottoms rate from the two towers:

$B_W = 99.00$

$B_P = 1.00$

(d) Equilibrium Vapor Concentrations. The equilibrium vapor concentration of the feed, and the lean and rich decantor streams is needed to estimate the minimum vapor rates. To find the equilibrium vapor concentration of the feed we assumed that the feed will enter the tower at 15 psia (775.7 mm Hg.). First we estimate the equilibrium temperature; try t = 220°F (104.4°C).

From Eq. (17): $A = 0.270$; from Eq. (18) $B = 1.573$.

From Eq. (19): $p^*_{phenol} = 48.6$ mm Hg; from Eq. (20): $p^*_{H_2O} = 889.2$ mm Hg.

Using Eqs. (12) & (13): $Z_A = 1.002$, $Z_B = 25.294$

Using Eq (14): $Y_A = 1.161$, $Y_B = 0.016$

Because $Y_A + Y_B > 1$, we must try a lower temperature. A plot of temperature against the sum of the vapor mole fractions is useful in finding the correct equilibrium temperature.

On trying $t_f = 212.7°F$ (100.4°C) we get

$A = 0.272,\ B = 1.588,$

$P^*_{phenol} = 40.45,\ P_{H_2O} = 771.5,$

$Z_A = 1.002,\ Z_B = 26.065,$

$Y_A = 0.9865,\ Y_B = 0.0135$

$Y_A + Y_B = 1.000.$

The vapor composition in equilibrium with the feed is therefore $Y^*_f = 0.9865$ at the boiling point of the feed which is 100.4°C.

Similarly we find that $Y^*_R = 0.9773$ at 214.5°F and $Y^*_L = 0.9822$ at 212.7°F.

(e) Minimum Vapor. At the feed tray on the water tower using Equation (4):

$$V_{min} = 1 \times (0.0001 - 0.99)/(0.9865 - 0.99) = 283 \text{ moles/100 moles feed}$$

At

At the top of the water tower using Equation (5):

$$V_{min} = 1 \times (0.0001 - 0.9835)/(0.9822 - 0.9835) = 756$$

At the top of the phenol tower using Equation (7):

$$V_{min} = \left\{100 \times (0.6754 - 0.99) + 99 \times (0.99999 - 0.6754)\right\} /(0.9773 - .6754)$$

$$= 2.234$$

If we use a steam rate of 4/3 of the minimum,

$$V_W = 756 \times 4/3 = 1{,}008 \text{ moles/100 moles feed}$$

and

$$V_P = 2.234 \times 4/3 = 2.979 \text{ moles/100 moles feed}$$

Reflux Rate and Overhead Composition. The reflux rates to the two towers are taken from Equation (8):

$$R_W = 1{,}008 + 99 - 100 = 1{,}007$$

$$R_P = 2.979 + 1 = 3.979$$

The composition of the vapors leaving the top trays is taken from Equation (9):

$$Y_{W,N} = (100 \times 0.99 + 1007 \times 0.9835 - 99 \times 0.99999)/1008 = 0.9825$$

$$Y_{P,N} = (4 \times 0.6754 - 1 \times 0.0001)/2.979 = 0.9068$$

(g) Water Tower Stages. Stage 1 (reboiler) $x_1 = x_B = 0.99999$. If the pressure drop per stage is taken to be 0.25 psi and for an estimated 16 stages, the pressure in the reboiler will be 15 + (16-1) x 0.25 = 18.75 psia. Using the equilibrium calculation method, we find $y_1 = 0.99992$ and $t_1 =$ 224.5°F. The liquid composition of the next stage is taken from Equation (10):

$$x_2 = (99 \times 0.99999 + 1008 \times 0.99992)/(1007 + 100) = 0.99993$$

The procedure

The procedure is repeated for each stage. The feed is introduced on the tray where x_n falls below x_f, and the top tray is reached when $y_n < y_N$ (see f above). The results are shown below:

Stage	x_n	y_n	t°F	P psia
1	0.99999	0.99992	224.5	18.75
2	0.99993	0.99978	223.8	18.50
3	0.99980	0.99957	223.1	18.25
4	0.99961	0.99929	222.4	18.00
5	0.99935	0.99877	221.6	17.75
6	0.99888	0.99779	220.9	17.50
7	0.99799	0.99617	220.1	17.25
8	0.99651	0.99376	219.3	17.00
9	0.99432	0.99075	218.4	16.75
10	0.99158	0.98783	217.6	16.5
11	0.98892	0.98553	216.8	16.25

Since $x_{11} < x_f$, stage 11 is the feed stage and Equation (11) is used for x_{n+1}

12	0.98650	0.98376	216.0	16.00
13	0.98473	0.98276	215.2	15.75
14	0.98374	0.98219	214.4	15.50

y_{14} is less than y_N (0.9825) so stage 14 is the top stage.

(h) Phenol Tower Stages. Stage 1 (reboiler) $x_1 = x_B = 0.0001$. For an estimated 8 plates the pressure in the reboiler is 15 + (8-1) x 0.25 = 16.75 psia. Using the equilibrium calculation method, we find $y_1 = 1.685\text{x}10^{-3}$ at 366.5°F. The liquid composition of stage 2 is taken from Equation (10):

$$x_2 = (1 \times 0.001 + 2.979 \times 1.685 \times 10^{-3})/(3.979) = 1.286 \times 10^{-3}$$

The results for the other stages are shown below:

Stage	x_n	y_n	t°F	P psia
1	$1\text{x}10^{-4}$	$1.685\text{x}10^{-3}$	366.5	16.75
2	$1.286\text{x}10^{-3}$	$2.14\text{x}10^{-2}$	364.4	16.50
3	0.0161	0.2263	349.5	16.25
4	0.1694	0.8298	274.9	16.00
5	0.6211	0.9736	219.1	15.75

y_5 is greater than y_n (0.9068) so stage 5 is the top stage.

A water tower of 14 theoretical stages, and a phenol tower of 5 theoretical stages yield the desired separation. The graphical method of Reference 24 gave 15 and 6 1/2 stages respectively. The steam rate required to achieve the desired vapor rate in each tower is calculated from a heat balance. The latent heat of water at 18.75 psia is 962 Btu/lb, and of phenol at 16.75 psia is about 205 Btu/lb. If, for example, we use 300 psig steam superheated to 600°F with a latent heat of 921 Btu/lb., then the steam rate per 100 lb mole feed for the water column = 1,008 x 962/921 = 1,053 lb mole steam and for the phenol column = 2.98 x 205 x 94/(18 x 921) = 3.5 lb mole steam. Sizing the columns, reboilers and condensers is discussed in Section 7.

Design Characteristics

(a) Phenol Tower

The phenol concentrations in coal conversion condensates are on the water side of the azeotrope, and the main feed is to the water tower. The reflux from the decantor to the phenol tower enters at a rate of about 1% of the main feed rate, and at a concentration of 70-75% phenol by mass.

Steam requirements for the coal conversion condensates are about 0.2 lbs per 100 lb feed to the water tower, and about 4 theoretical stages will generally produce a 99.9% phenol product. Consequently, capital and operating costs for the phenol tower are low.

(b) Water Tower

The pinch condition for our test calculations based on typical coal conversion condensates invariably occurred at the feed plate so the minimum steam rate for this tower is given by Equation (4). Although they are not as high as those in the example, the minimum steam rates are still excessive at about 100-150 lbs/100 lbs feed. This is illustrated in Figure 3-6; note also that steam duties increase as the phenol load increases.

Some reduction in steam duty will be obtained when the required phenol removal efficiency is lowered. However, at 80% removal efficiency the minimum steam rate is about 84 lb steam/100 lb feed. Further reductions in steam may be obtained by operating at elevated pressures, or by decreasing the decantor temperature. These reductions are not significant and incur additional capital and operating costs.

Steam rates for ammonia stripping are at least an order of magnitude lower than required for phenol removal, so even if ammonia separation could be achieved in the phenol distillation system, overall steam rates would still be excessive. At \$2.50 per 10^6 Btu, the cost for the steam to the water tower amounts to \$25 to \$30 per 10^3 gal condensate treated, and it is clear that an alternative means of breaking the phenol water azeotrope must be used.

3.2 Phenol Recovery by Solvent Extraction

In Figure 3-8 we show an idealized solvent extraction system. The feed water is contacted counter-currently with liquid solvent in an extraction unit so that the solute (phenol) is selectively transferred to the solvent or extract phase. The solvent must not mix with water. One measure of the quality of a solvent is the "distribution ratio," k, defined by

$$k = \frac{\text{concentration of phenol in solvent}}{\text{concentration of phenol in water}} \qquad (22)$$

Solvents that have been used in the past include benzene and kerosene. For benzene $k \simeq 2.3$ which is quite low. Two modern solvents are isopropyl ether ($k \simeq 45$) and normal butyl acetate ($k \simeq 70$).

Part of the complexity of extraction processes is the large number of possible solvents that should be evaluated. Mixed solvents can be used[8]. Published information on distribution coefficients refers to phenol. We know of no tests on actual coal conversion wastewaters to determine what other materials are extracted by any particular solvent. And yet information such

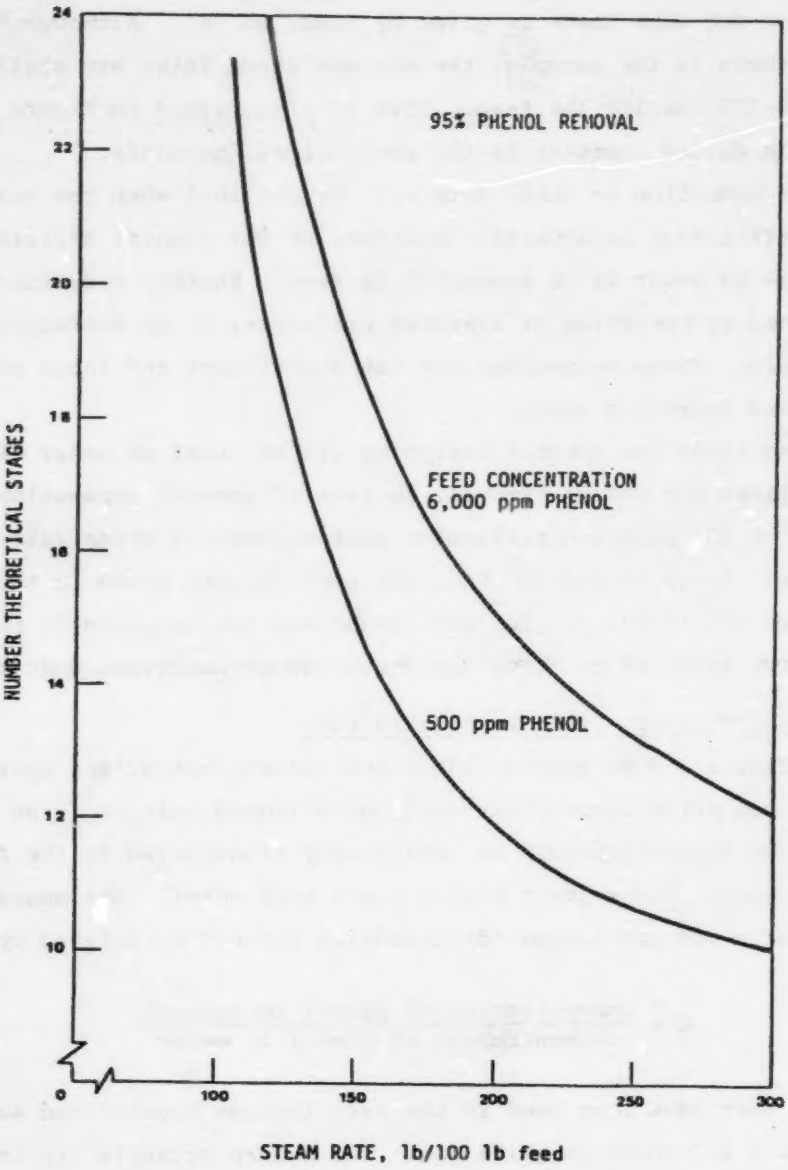


Figure 3-6. Steam rates and theoretical stages in water tower for phenol removal by distillation.

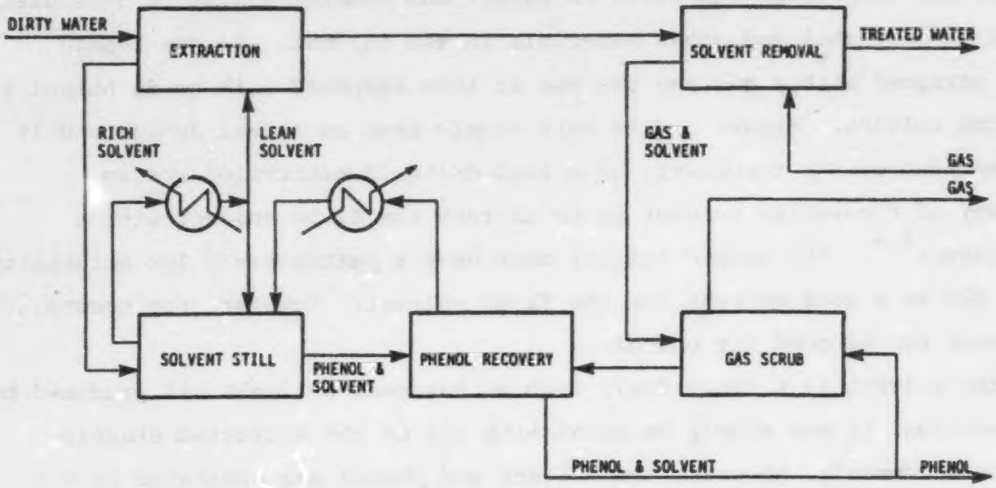

DIRTY WATER
EXTRACTION
SOLVENT REMOVAL
TREATED WATER
RICH SOLVENT
LEAN SOLVENT
GAS & SOLVENT
GAS
GAS
SOLVENT STILL
PHENOL & SOLVENT
PHENOL RECOVERY
GAS SCRUB
PHENOL & SOLVENT
PHENOL

Figure 3-7. Phenosolvan process. (References 34 & 35)

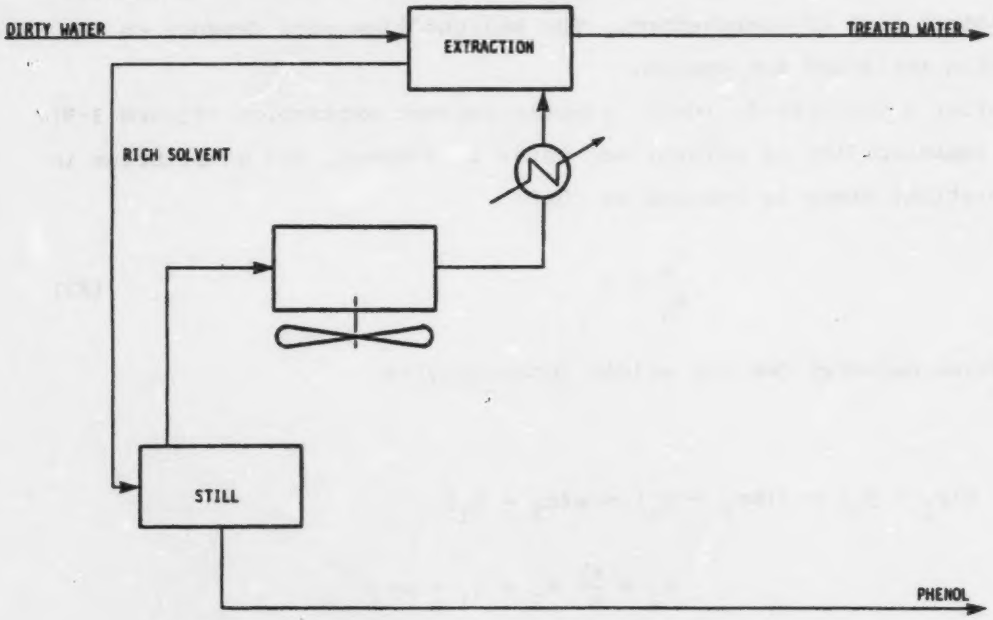

DIRTY WATER
EXTRACTION
TREATED WATER
RICH SOLVENT
STILL
PHENOL

Figure 3-8. Idealized solvent extraction.

as the distribution ratio for BOD is what determines whether biological treatment is or is not required subsequent to extraction.

After extraction residual solvent must usually be removed from the water (no solvent is completely insoluble in water) and something must be done with the solution of phenol and other materials in the solvent. In one design water is stripped with a gas and the gas is then scrubbed with crude phenol to recover the solvent. Figure 3-8 is more simple than an actual design and it gives some idea of the complexity of a liquid-liquid extraction system. Another way of recovering solvent is to extract the first solvent with a second solvent[3,6]. The second solvent must have a particularly low solubility in water and be a good solvent for the first solvent. However, the second solvent need not be good for phenol.

If the solvent is a cheap fuel, such as kerosene or light oil produced by coal conversion, it may simply be burnt with all of the extracted organic matter. More commonly, however, the solvent and phenol are separated by distillation. This means that two additional attributes of a good solvent are a high volatility relative to phenol and a low latent heat of vaporization.

The energy consumed in solvent extraction is mostly used to distill solvent and is approximately the product of the solvent flow rate and the solvent latent heat of evaporation. The solvent flow rate depends on the distribution ratio and the design.

Consider a simplified, ideal, counter-current extraction (Figure 3-9). Complete immiscibility of solvent and water is assumed, and equilibrium in each theoretical stage is assumed so that:

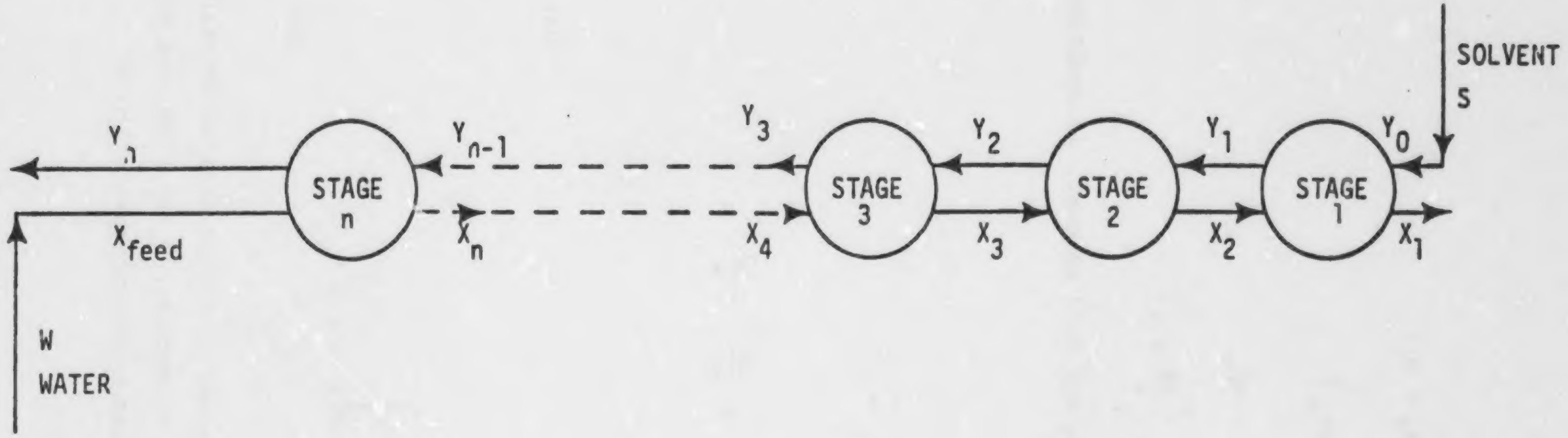
$$\frac{y_n}{x_n} = k \qquad (23)$$

Material balances for the solute (phenol) give

Stage 1

$$s(y_1 - y_o) = s(kx_1 - y_o) = w(x_2 - x_1)$$

$$x_2 = \frac{sk}{w} x_1 + x_1 - sy_o$$


SOLVENT
S
Y_0
STAGE 1
X_1
Y_1
X_2
STAGE 2
Y_2
X_3
STAGE 3
Y_3
X_4
Y_{n-1}
X_n
STAGE n
Y_n
X_{feed}
W
WATER

w = water feed rate, 10^6 lb/hr
s = solvent feed rate, 10^6 lb/hr
y = phenol concentration in solvent, ppm
x = phenol concentration in water, ppm

Figure 3-9. Ideal counter-current liquid-liquid extraction.

Stage 2

$$s(y_2 - y_1) = sk(x_2 - x_1)$$

$$= sk\left(\frac{skx_1}{w} - sy_o\right) = w(x_3 - x_2)$$

$$= w\left(x_3 - \frac{skx_1}{w} - x_1 + sy_o\right)$$

$$x_3 = \frac{sk}{w}\left(\frac{skx_1}{w} - sy_o\right) + \frac{skx_1}{w} + x_1 - sy_o$$

$$= \left(\frac{sk}{w}\right)^2 x_1 + \frac{sk}{w} x_1 + x_1 - sy_o \left(\frac{sk}{w} + 1\right)$$

If y_o, the concentration of phenol in the feed solvent, is negligible, one obtains

Stage n

$$\frac{x_f}{x_1} = \left(\frac{sk}{w}\right)^n + \ldots + \frac{sk}{w} + 1$$

so

$$\frac{sk}{w}\,\frac{x_f}{x_1} = \left(\frac{sk}{w}\right)^{n+1} + \ldots + \frac{sk}{w}^{2} + \frac{sk}{w}$$

and, by subtraction:

$$\frac{x_f}{x_1} = \frac{\left(\frac{sk}{w}\right)^{n+1} - 1}{\frac{sk}{w} - 1} \qquad (24)$$

or

$$\frac{\log\left[\left(\frac{x_f}{x_1}\right)\left(\frac{sk}{w} - 1\right) + 1\right]}{\log \frac{sk}{w}} = n + 1 \qquad (25)$$

Equation (25) relates the number of stages, n, to the desired extraction ratic x_f/x_1, the extractive ability of the solvent, k, and the flow rate ratio of solvent to water, s/w. Figure 3-10 is a graphical representation of Equation (25).

On Figure 3-10, the lines have been labelled "percent removal."

$$\text{Percent removal} = 100 \; \frac{x_f - x_1}{x_f} .$$

For 99.9% removal: $\frac{x_f}{x_1} = 1000$

99% removal: $\frac{x_f}{x_1} = 100$

95% removal: $\frac{x_f}{x_1} = 20$

80% removal: $\frac{x_f}{x_1} = 5$

In Figure 3-10 it is shown that at any given solvent-to-water rate and desired percent removal, the number of stages will decrease as the solvent rate is increased. With fewer stages the extraction column and its cost will be smaller; however, all of the solvent has to be evaporated to separate it from the phenol, and increasing the solvent rate increases the cost of the still and of the energy. Thus, each design requires an economic optimization that must be repeated for each solvent and for each percent removal.

There is probably a lower limit to the solvent rate which tells us something about the energy consumption. Good contact is required between the water and the solvent. Contacting means mixing followed by settling in many stages while the solvent and water flow counter-currently. Yet another attribute of a good solvent is that its density differs appreciably from that of water so that the water can settle. If the wastewater is contaminated with emulsifying agents such as detergents, the whole process may not work at all. Good contact and good separation cannot be achieved if the solvent-to-water ratio, s/w, is too low. As a reasonable example, let us suppose that the minimum s/w is 0.1, no matter how large the distribution ratio, k. If the energy consumed is 190 Btu/lb solvent, then a solvent-to-water ratio of 0.1 means 158 x 10^3 Btu/10^3 gallons of water. This will apply only if a good solvent is available. If k gets as low as 2.3 (for benzene), economic optimization will result in s/w >0.1. In a preliminary study[33] a ratio about 0.7 was found to be

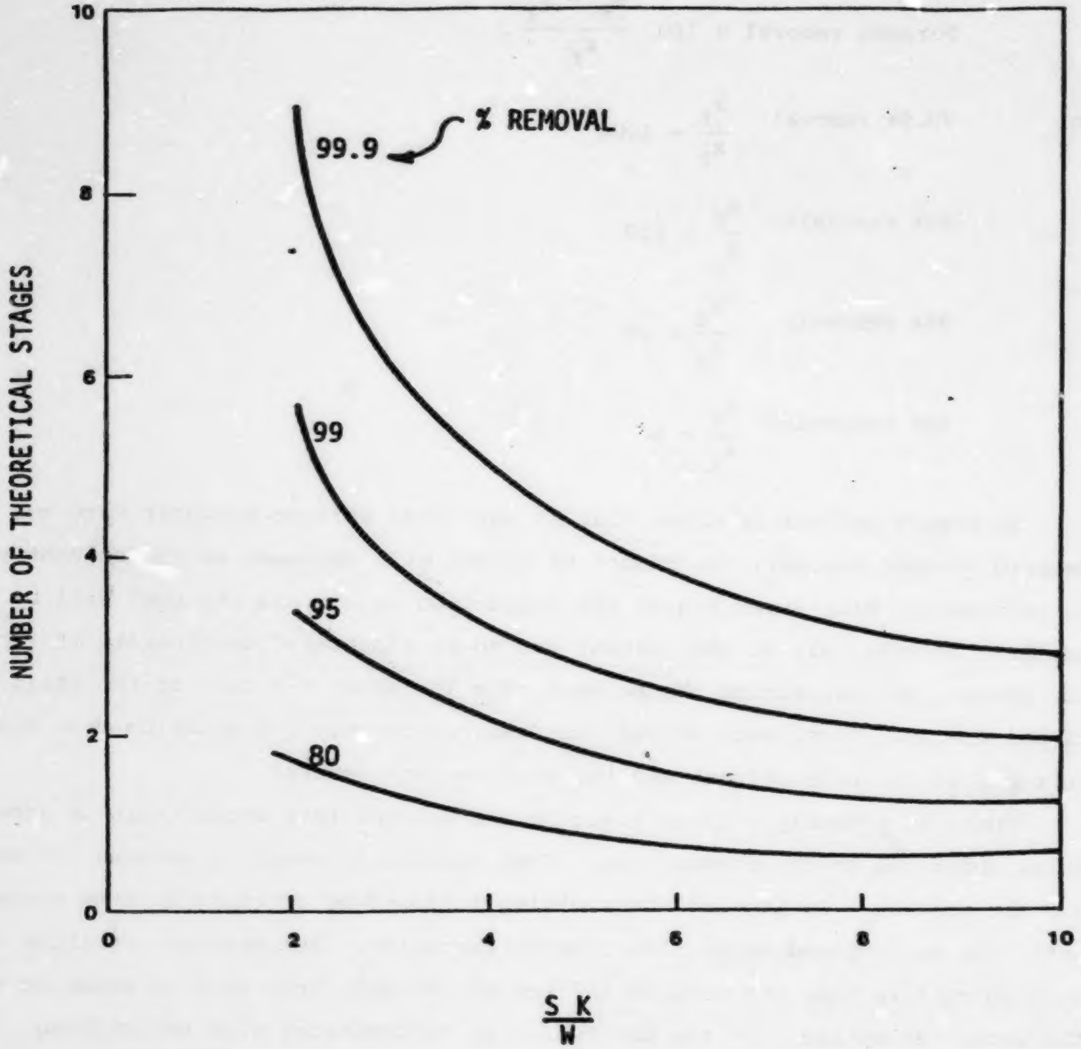


Figure 3-10. The extraction equation.

optimum. In this case the energy consumption is about 1,000 x 10^3 Btu/10^3 gallons. The optimum for good solvents ($k > 20$) will be found in a following example.

Sizing Extraction Equipment

Extraction equipment consists of a mixing or contacting section, and a settling or phase separation section. The size of each section is determined by the mean residence time required for the respective function.

In the contacting stage the two immiscible liquids are agitated to produce a dispersion of droplets and a continuous phase, between which mass transfer occurs. The residence time is determined by the mass transfer rate, which in turn is governed by the transport properties of the species in solution and the characteristics of the droplets. The droplet characteristics are functions of the geometry, size and materials of construction of the mixer, the intensity of agitation and the phase fraction and fluid properties including viscosities, densities, surface energies and concentration of dissolved solutes[15]. The residence time in the settler is governed essentially by the rate of droplet coalescence. Considerable work to predict droplet breakage and coalescence rates has been published[16,17], but even trace impurities can have a profound effect on the process. Because most researchers have worked with extremely pure systems, their results cannot be applied to an industrial situation.

The volumes of the mixing and settling sections can be calculated from the residence time t in each section:

$$V \text{ ft}^3 = 2.7 \times 10^{-4} w\ (1 + s/w)\ t \text{ min} \qquad (26)$$

for w in lb/hr wastewater feed.

If residence time information is not available, values of 5 minutes for the mixer and 20 minutes for the settler may be used.

Designs may be based on horizontal mixer settlers as used and supplied by Lurgi[14]. These are probably convenient for pilot scale and preliminary designs, but in some instances devices using less floor space may be desirable. The Scheibel or rotating disc type columns may be used. Designs can be obtained from Chem Pro[13].

3.2.1 Solvent Regeneration

In Figure 3-11 we have shown a possible arrangement for a solvent regeneration section. The solvent is distilled off the solvent-phenol-water mixture, condensed and recycled to the extraction stage. Reflux and reboil steam are used. Vapor-liquid equilibria data for the ternary system which are required for distillation column design may be found using numerical procedures for multicomponent systems[36].

While ternary vapor-liquid data have been published for some systems, they are usually restricted to specific temperature and/or pressure conditions[18]. If binary data are available, they may be used to generate binary coefficients for the van Laar or Wilson equations[27], which in turn may be used for estimating coefficients for the ternary system[28,36]. Experimental data for at least two temperatures are useful to estimate the temperature dependence of the coefficients, and to check whether the chosen system of equations is applicable. The procedure is tedious and involves a trial calculation for composition and temperature on each plate, and a mass balance on each column. We attempted the calculations using the van Laar two suffix equations for the ternary vapor-liquid system but were unsuccessful, apparently because of the high nonideality of the butyl acetate-water subsystem.

Approximately the system may be treated as a binary mixture. In estimating the number of stages for separation, the binary system with the smallest relative volatility should be chosen. When the solvent is butyl acetate, equilibria data for butyl acetate-phenol should be used[18]. We assumed that all of the water in the ternary mixture would leave the column with the phenol, so that our design for the phenol column would be safe. The configuration for the solvent regeneration is consequently different from the one usually shown for the Lurgi Phenosolvan system, but it is adequate for estimating purposes.

Vapor-liquid equilibria for butyl acetate-phenol

The van Laar coefficients at 44.4°C are[18]

A (butyl acetate) = -0.75

and B (phenol) = -0.95 (27a)

At other than 44.4°C the van Laar coefficients can be determined by assuming the product of the van Laar coefficient and the absolute temperature to be constant. Thus:

A (butyl acetate at t°C) = -0.75 x (44.4 + 273)/(t + 273)

B (phenol at t°C) = -0.95 x (44.4 + 273)/(t + 273)

(27b)

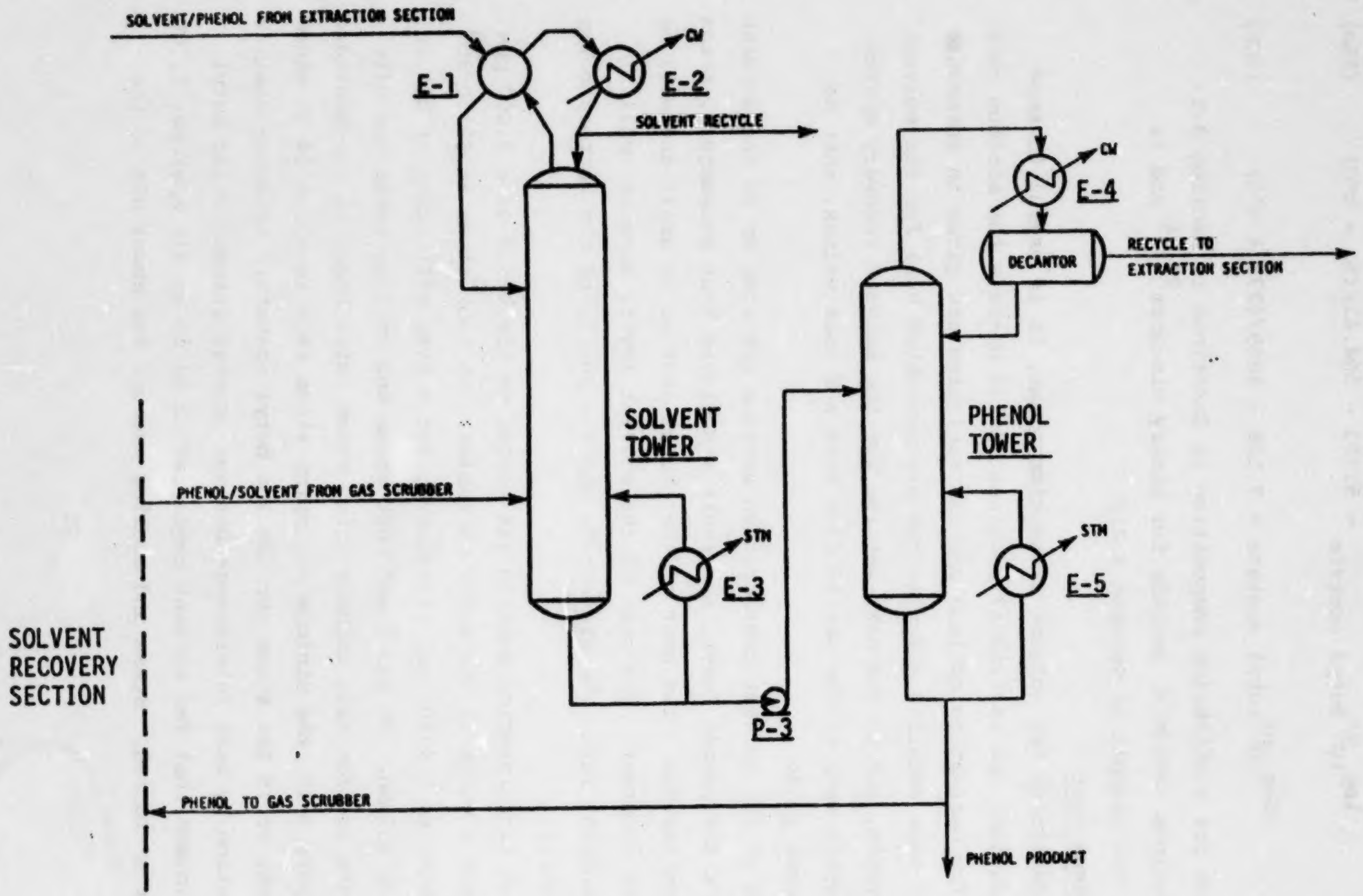

SOLVENT/PHENOL FROM EXTRACTION SECTION
E-1
CW
E-2
SOLVENT RECYCLE
CW
E-4
DECANTOR
RECYCLE TO EXTRACTION SECTION
SOLVENT TOWER
PHENOL TOWER
PHENOL/SOLVENT FROM GAS SCRUBBER
STM
E-3
STM
E-5
SOLVENT RECOVERY SECTION
P-3
PHENOL TO GAS SCRUBBER
PHENOL PRODUCT

Figure 3-11. Possible arrangement of solvent regeneration section for phenol extraction.

These values are used in the van Laar Equations (12) & (13) to determine vapor or liquid equilibrium compositions. The vapor pressures may be evaluated from Equation (19) for phenol, and for butyl acetate from:

Up to 130°C $$\log_{10} p^*_{\text{butyl acetate}} = 5.183 - 504.41/(93 + t°\text{C}) \qquad (28a)$$

Above 130°C $$\log_{10} p^*_{\text{butyl acetate}} = 7.528 - 1859/(273 + t°\text{C}) \qquad (28b)$$

The calculation for equilibrium composition is described in Section 3.1. Tower design follows textbook methods for binary mixtures[24,36] and is illustrated by the example in Section 3.2.3.

Design for minimum cost

Prior to designing the solvent extraction plant, it is useful to know under what conditions the individual sections should operate for minimum cost. Rapid methods for estimating optimum process variables are given in Reference 38. Results of some detailed calculations are presented here for the solvent regeneration system, and in the next section for the solvent recovery system. Although they apply only to the stated flow rate and cost values, they do serve as a general guide.

The costs of the solvent regeneration section are made up of the solvent fractionator and the phenol tower, and their associated heat exchangers, steam and cooling requirements. The cost of the phenol section is small and will be considered to be constant. The cost of the solvent tower, however, will depend on the solvent rate, the steam rate and the purity of the bottoms going to the phenol still.

The solvent fractionation section was costed on the basis of a 2,000 ppm phenol stream for a range of the above variables. We took steam at $\$2.50/10^6$ Btu, cooling water at $12¢/10^3$ gal circulated, and a tray efficiency of 50% in the distillation column. It was found that steam and cooling costs dominate and minimum costs are for tall columns using steam rates close to the minimum. As shown in Figure 3-12, the minimum stripping steam rate is about 14 lb steam per 100 lbs feed, or 15 lbs steam per 100 lbs butyl acetate. Assuming maximum energy conservation by heat interchange between process streams using butyl acetate, the minimum cost for solvent regeneration is about $(6 s/w) per 1,000 gals wastewater extracted. Steam and cooling account for about 85% of the total costs.

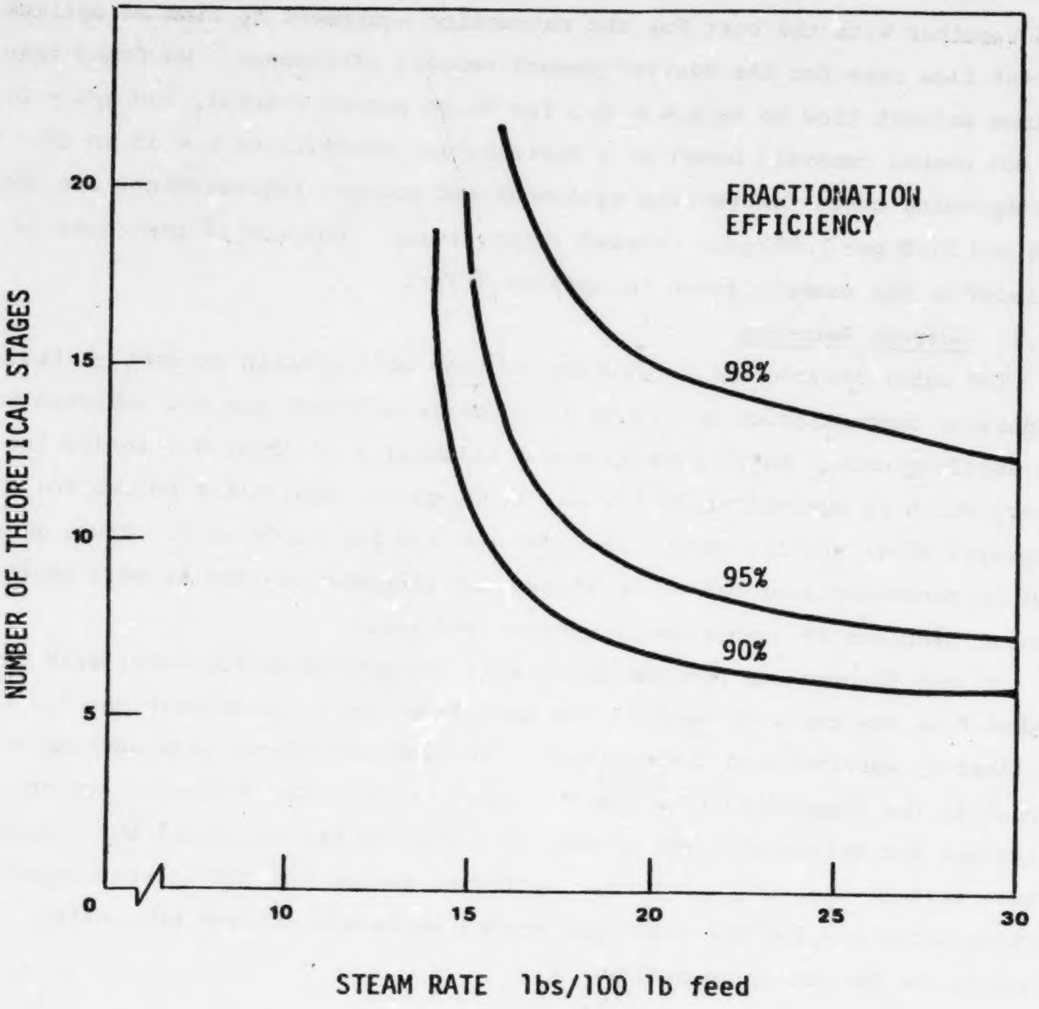


Figure 3-12. Theoretical stages for solvent regeneration fractionation

Because solvent recovery costs (next section) are virtually independent of the solvent-to-liquid flow rate, the cost for solvent regeneration can be used together with the cost for the extraction equipment to find an optimum solvent flow rate for the desired phenol removal efficiency. We found this optimum solvent flow to be s/w = 0.3 for 99.9% phenol removal, and s/w = 0.1 for 80% phenol removal, based on a distribution coefficient k = 10 to 20. The corresponding costs (extraction equipment and solvent regeneration) are about \$2.0 and \$1.0 per 1,000 gals treated respectively. One set of cost data is included in the example given in Section 3.2.3.

3.2.2 Solvent Recovery

The water leaving the extraction section will contain solvent at its solubility concentration or higher if adequate settling was not achieved in the settling unit. Butyl acetate has a solubility of about 0.7 lb/100 lb water, which is equivalent to \$22 per 1,000 gals. Equivalent values for isopropyl ether are 1.2 lb/100 lb water and \$16 per 1,000 gals. Thus, solvent must be recovered from the water stream for economic reasons as well as to prevent problems in downstream treatment and reuse.

In the Phenosolvan process solvent is stripped from the water with gas, washed from the gas with some of the wastewater prior to extraction, and then polished by washing with crude phenol. We have considered only washing with phenol in the simplified flow sheet (Figure 3-13). The following design procedure for determining the number of stages in the stripping and scrubbing towers will be used to find a cost optimized design for the solvent recovery section using a 2,000 gpm 6,000 ppm phenol wastewater stream when using nitrogen as the stripping medium.

Design Procedure

A material balance around the lower section of the stripping or scrubbing tower, up to plate n, yields:

$$x_{n+1} = G(y_n - y_o)/L + x_1 \qquad (29)$$

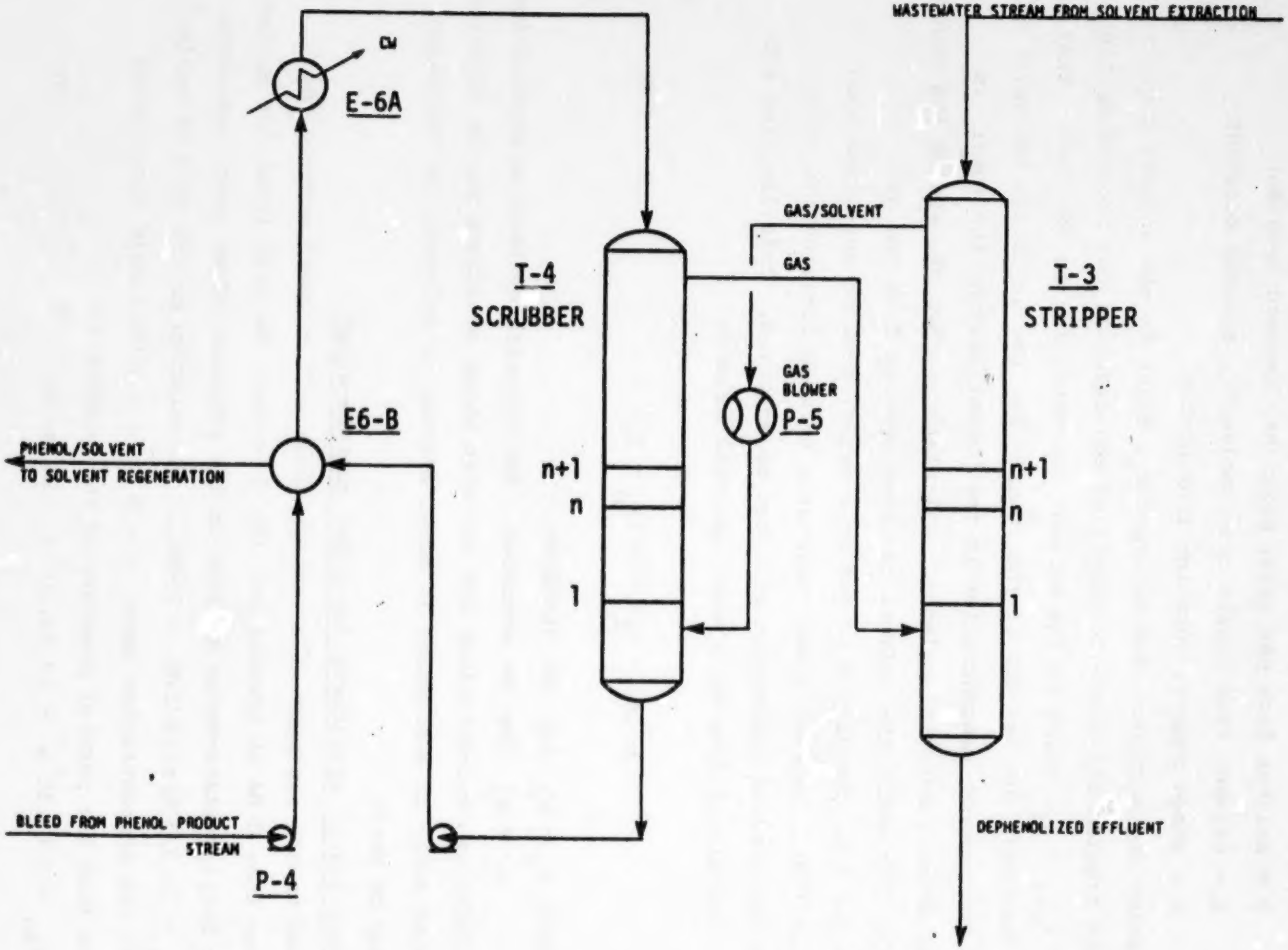

CW
E-6A
WASTEWATER STREAM FROM SOLVENT EXTRACTION
GAS/SOLVENT
GAS
T-4
SCRUBBER
T-3
STRIPPER
GAS
BLOWER
P-5
E6-B
PHENOL/SOLVENT
TO SOLVENT REGENERATION
n+1
n
1
n+1
n
1
BLEED FROM PHENOL PRODUCT
STREAM
P-4
DEPHENOLIZED EFFLUENT

Figure 3-13. Solvent recovery section of Phenosolvan process.

where x mole ratio solvent in liquid

y = mole ratio solvent in gas

G = solvent free gas rate, moles/hr, assumed constant

L = solvent free liquid rate, moles/hr, assumed constant

n = stage number, counting from bottom.

In designing the stripper, the value of x_1, which is the solvent concentration in the treated effluent, is specified and calculations proceed up the tower until $x_{n+1} > x_f$, which is the solvent concentration in the feed. Tray n is then the feed tray and the top of the tower. For the scrubber, the value of x_1, which is the solvent concentration in the phenol leaving the tower, is found from an overall material balance. Calculations then proceed up the tower using Equation (29) until the solvent has been removed from the gas.

A value for L/G, the liquid to gas mole ratio, must be specified when using Equation (29). In each tower there will be some limiting L/G value beyond which the desired separation will not be achieved. This limiting L/G value may be calculated from an overall material balance:

$$L\ (x_f - x_1) = G\ (y_n - y_o) \tag{30}$$

by substituting $y_n = y_f^*$ for the stripper,

and $x_1 = x_o^*$ for the scrubber. The asterisk denotes an equilibrium value. Equilibrium concentrations for use with these equations may be obtained from published data, if available; if butyl acetate is solvent, the following procedure may be used:

Stripper vapor-liquid equilibria for butyl acetate-water

The feed to the stripper will contain about 0.7 lb butyl acetate and probably less than 0.04 lb phenols per 100 lb water. We will treat the system as a binary butyl acetate-water mixture in the presence of an inert saturated gas with $x_f = (0.7/100)x(18/116) = 0.0011$. Correlation of the data of Weller[18] for 112°F in the concentration range $x = 0$ to $x = 0.0011$ mole ratio butyl acetate show that the partial pressure of the solvent is:

$$p_{BA} = 7.68.10^6 x^2 + 19.44.10^3\ x, \text{ in mm Hg} \tag{31}$$

x is the liquid phase concentration, moles butyl acetate per mole water. The mole ratio in the gas phase can be calculated from

$$y = p_{BA}/(P - p_{BA}) \qquad (32)$$

where P is the total pressure in the tower.

Scrubber vapor-liquid equilibria for butyl acetate-phenol

Butyl acetate is completely miscible with phenol and concentrations of up to 70% butyl acetate by mass may be reached in the scrubber. Correlation of the data of Weller[18] for 112°F give the partial pressure of the solvent as

$$p_{BA} = 9.5 \quad x/(1 + x) \qquad x < 0.2 \qquad (33a)$$

and

$$p_{BA} = 34.5 \left\{ x/(1 + x) \right\}^{1.76} \quad 0.2 < x < 10 \qquad (33b)$$

Here x is moles butyl acetate per mole phenol in the liquid phase. The corresponding mole ratio in the gas phase is taken from Equation (32).

Design Characteristics

The limiting L/G rates in the stripper and scrubber are found from Equation (30) and the appropriate vapor-liquid equilibrium equation for acetate. For the stripper, $x_f = 0.0011$, $y_f{}^* = 0.0415$ (Equations 31 & 32) so

$$(G/F)_{min,\ stripper} = (0.0415 - 0)/(0.0011 - 0) = 0.026$$

For the scrubber if $x_f = o_o$ and $y_o = 0.0415$, then $x_o{}^* > 10$ (Equations 33b & 32) so

$$(P/G)_{min,\ scrubber} < (0 - 0.0415)/(0 - 10) < 0.004$$

where F = water feed rate to stripper, lb moles/hr

P = phenol feed rate to scrubber, lb moles/hr. The ratio for the scrubber probably falls below the limiting value for good contacting in a packed column, and this should be checked for a final design.

The number of theoretical stages decreases as the flow rates are increased above the minimum (Figure 3-14). The number of stages also decreases as the specified removal efficiency decreases. The value of butyl acetate remaining in the water when stripping to 90, 99 and 99.9% efficiency is about $2.2, $0.22 and $0.02 respectively. Provided there are no other constraints on the solvent concentration remaining in the water, the stripping efficiency will be determined by system economics. The efficiency of the scrubber will generally be between 99.9 and 99.99%; the number of stages does not change significantly in this range.

Design for Minimum Cost

The solvent recovery section is treated as an independent system and costed for various conditions on the basis of a 2,000 gpm, 6,000 ppm phenol stream after removing 95% of the phenols by extraction. Butyl acetate is the solvent.

The capital cost of the stripper depends on the solvent concentration in the feed, the stripper efficiency and the gas rate. The feed concentration is fixed, and the other two parameters were varied over the range shown in Figure 3-14. The operating costs are determined by the power required to pump the gas and the value of the solvent that is not recovered. A cost of 38¢/lb butyl acetate was used.

The cost of the scrubber is dependent essentially on the phenol flow rate and the volume of gas to be treated. The cost of the two heat exchangers (Figure 3-13) was included in the costs; returning the phenol stream to the solvent regeneration section was not included.

In figuring capital costs for the towers, tray columns at 50% stage efficiency were assumed. We do not anticipate costs for packed columns to differ significantly. The contribution of capital cost to the annual total cost for solvent recovery was assessed at 19%; 15% for amortization and 4% for maintenance.

The minimum cost for solvent recovery is 30¢ per 1,000 gallons. This was obtained with a stripper recovery efficiency of 99.9%, for a gas-to-water ratio (G/F) of 0.05 to 0.055 in the stripper and for a phenol-to-gas ratio (P/G) of 0.05 in the scrubber. The total cost is divided: 56% for stripping, 8% for solvent losses, 32% for gas blowing and 4% for scrubbing. Costs are not strongly dependent on (G/F) and (P/G). As (G/F) is increased, scrubber costs decrease, but gas blowing costs increase. Scrubbing costs make only a small contribution to the total costs so dependence on (P/G) is weak. A (P/G)

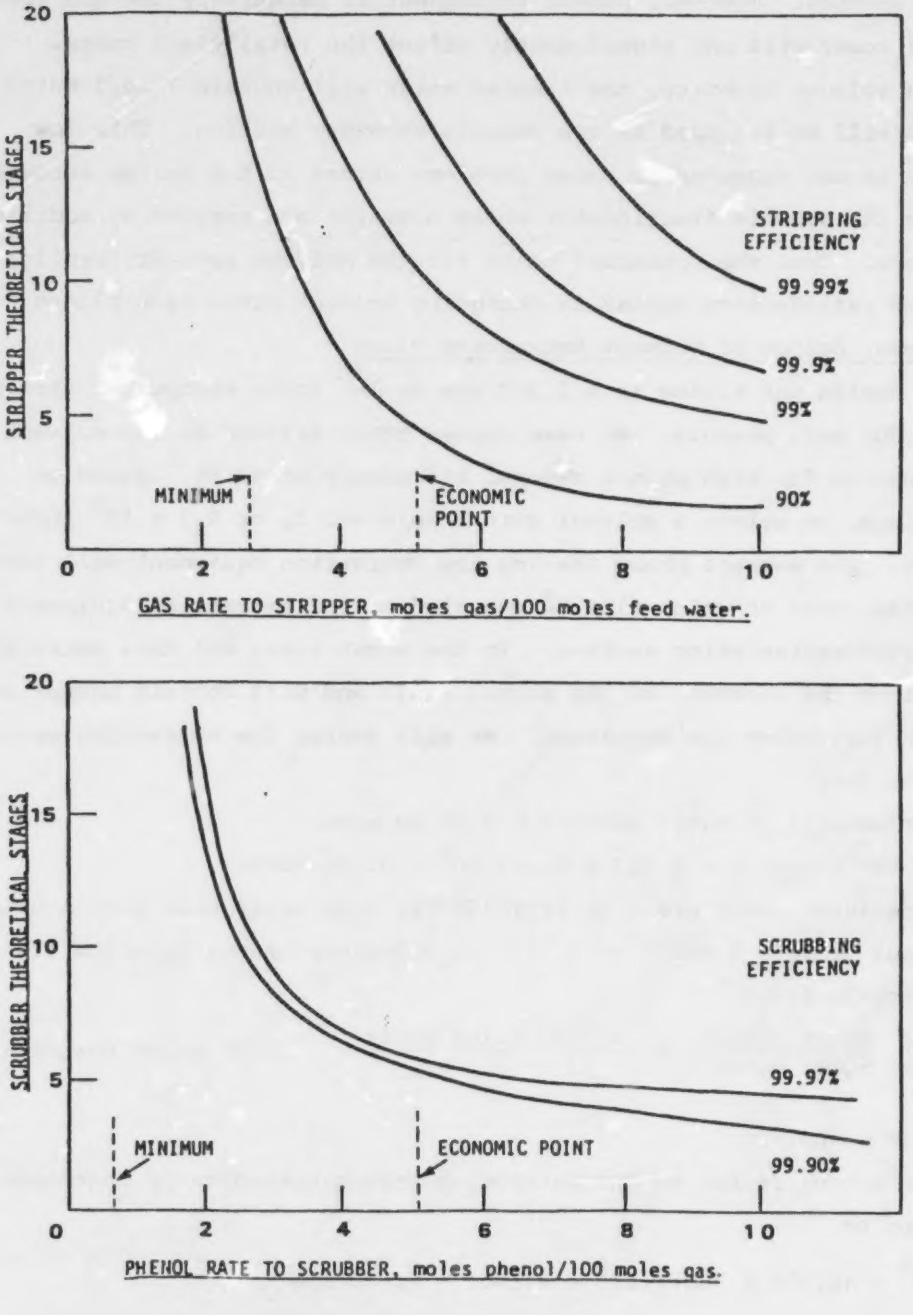


Figure 3-14. Theoretical stages for water stripping and gas scrubbing in solvent recovery section.

value of 0.1 requires a phenol circulation rate of two to three times the product phenol rate, and it will increase the cost of the phenol tower in the regeneration section. However, phenol throughput is relatively low and costs of the phenol tower will not significantly affect the total plant costs.

At 99.9% solvent recovery, the treated water will contain 7 mg/l butyl acetate which will be stripped in the ammonia recovery section. This low concentration is not expected to cause problems either in the sulfur recovery section or in the ammonia fractionator where organics are removed by addition of caustic soda. Thus the optimized costs for the solvent recovery section may be assumed satisfactory guides in designing solvent extraction plants.

3.2.3 Example: Design of Solvent Extraction Plant

In this design our source is a 2,000 gpm or 10^6 lb/hr wastewater stream containing 6,000 mg/l phenols. We have chosen butyl acetate as the solvent and we will design for high phenol removal efficiency of 99.9%. Based on earlier findings, we select a solvent rate of s/w = 0.3, or 0.3×10^6 lb/hr butyl acetate. The extract phase leaving the extraction equipment will contain dissolved water, most of which will be recycled to the extraction equipment from the solvent regeneration section. In the worst case, all this water will be recycled from the decantor on the phenol still and will contain phenol at a concentration just below the azeotrope. We will design the extraction system for this worst case.

Water solubility in butyl acetate = 2.7% by mass.

Total water recycled = $0.027 \times 0.3 \times 10^6 = 8{,}100$ lb/hr

If the decantor temperature is 68°F (20°C), this water will have a mole fraction phenol of (1 - 0.9832) or 0.0168 as calculated using Equation (1b). The phenol recycle is:

$$\frac{(0.0168)}{(1-0.0168)} \frac{\text{moles phenol}}{\text{moles water}} \times \frac{8{,}100}{18} \frac{\text{moles water}}{\text{hr}} = 7.69 \text{ lb moles phenol/hr}$$

or 723 lb phenol/hr.

The feed concentration to the extraction system consequently increases from 6,000 ppm to

$$x_f = 10^6 \times (6{,}000 + 723)/(10^6 + 8{,}100) = 6{,}670 \text{ ppm}$$

and for 99.9% removal from the original feed, the concentration of the treated water must be

$$x_1 = (1 - 0.999) \times 6{,}000 = 6 \text{ ppm}$$

The distribution coefficient for butyl acetate-phenol is about 65, but in view of the other constituents present in coal conversion condensates and the high overall removal we require, a value of k 10 is used. Experimentally determined k values should be used if available. Using the above values for x_f, x_1, s/w and k, we find from Equation (25) that 6 extraction stages are required. The actual number will equal the calculated number because we have used a conservative k value, and will use mixer-settlers that probably operate at close to equilibrium conditions.

Volume and Cost of Mixer-settlers

Using residence times of 5 minutes for the mixer and 20 minutes for the settler from Equation (26):

$$V_{mixer} = 2.7 \times 10^{-4} \times 10^{6} \ (1 + 0.3) \times 5 = 1{,}755 \text{ ft}^3 \text{ and}$$
$$V_{settler} = 1{,}755 \times 20/5 = 7{,}020 \text{ ft}^3$$

The vessel is 12 ft high with 27 ft sides and contains a 12 x 12 mixing partition. The volume of metal for the six vessels may be used to estimate the cost of the unit. A typical mixer-settler arrangement is given in Reference 39. If we use 1/2" metal plate for sides, top and bottom, and arrange the vessels in two back-to-back trains of three vessels each, about 600 ft^3 or 300,000 lb of metal are required. Assuming a cost factor of \$6 per lb, and an installation factor of 3.75 allowing for field fabrication, mixing motors, pumps, instrumentation, etc., the total installed cost will be about $\$6.8 \times 10^6$.

Solvent Regeneration (Figure 3-11)

The solvent still is designed to handle the full solvent and phenol load.

Solvent rate = $0.3 \times (10^6 + 8{,}100) = 302 \times 10^3$ lb/hr or 2,600 lb mole/hr

Phenolrate = $6{,}000 + 723 = 6{,}723$ lb/hr or 72 lb mole/hr

Water rate = $0.027 \times 302 \times 10^3 = 8{,}100$ lb/hr or 450 lb mole/hr

The main feed rate is the sum of the components = 3,122 lb moles/hr.

There will be secondary feed from the solvent recovery section consisting of phenol and butyl acetate. This feed does not significantly alter the design of the solvent fractionator because the phenol is relatively nonvolatile and will be removed directly with the bottoms and the butyl acetate has been accounted for in determining the main feed rate. The extra phenol must, however, be included in the design of the phenol still.

Solvent Fractionator (Figure 3-11)

The number of stages may be estimated on the basis of a binary phenol-butyl acetate mixture. Using the above feed rates we obtain

$$x_f = 2{,}600/(2{,}600 + 72 + 450) = 0.833$$

We require a virtually phenol-free solvent recycle, say less than 0.02 mole % impurities, and specify $x_D = 0.9998$. Since any butyl acetate that is not removed in the solvent still can be recovered from the phenol still decantor, a recovery efficiency of E = 95% is adequate. With a feed of F = 100 moles/hr, the overhead rate D is:

$$Dx_D = EFx_f$$

so

$$D = (0.95)(100)(0.833)/0.9998 = 79.15 \text{ moles/hr}$$

and by material balance the bottoms rate is

$$B = 100 - 79.15 = 20.85 \text{ moles/hr}$$

Calculation of equilibrium vapor compositions follows the procedure in the phenol tower design example, but using the van Laar coefficients A and B from Equation (27). The equilibrium temperature of the feed was found to be 277.5°F (136.4°C) at a pressure of 15 psia (775.7 mm Hg). At this temperature

$$A = -0.75 \times (44.4 + 273)/(136.4 + 273) = 0.5815 \text{ and}$$
$$B = -0.95 \times (44.4 + 273)/(136.4 + 273) = -0.7365$$

From

Equation (28b): $p^*_{\text{butyl acetate}} = 970.7$ mm Hg

Equation (19): $p^*_{\text{phenol}} = 178.4$ mm Hg

Equation (12): $Z_A = 0.9466$; Equation (13): $Z_B = 0.3401$

Equation (14): $y_A = 0.9466 \times 970.9 \times 0.833/775.7 = 0.9869$

and $y_B = 0.3401 \times 178.4 \times (1-0.833)/775.7 = 0.0131$

Since $y_A + y_B = 1.0$ the temperature is correct and $y^*_f = y_A = 0.9869$.

The minimum reflux ratio for the desired fractionation is:

$$
\begin{aligned}
R_{min} &= (x_o - y_f)/(y_f - x_f) \\
&= (0.9998 - 0.9869)/(0.9869 - 0.833) = 0.086
\end{aligned}
$$

In Section 3.2.1 we found that it is economical to keep the steam rate low. From Figure 3-12 a steam rate of 15 lb/100 lb feed or one mole steam per mole feed seems reasonable. The vapor rate for a feed of 100 moles/hr is, therefore, V = 100 moles/hr and the reflux ratio is:

$$R = (V/O) - 1 = (100/79.15) - 1 = 0.26$$

This is adequately above the calculated R_{min} value.

Stage calculations can be started at the bottom of the tower. The bottoms concentration is given by $x_B = (Fx_f - Dx_D)/B = (1-E)\ Fx_f/B = 0.200$. For a pressure drop of 0.25 psi per stage and an estimated 11 stages, the reboiler pressure is $15+(11-1) \times .25 = 17.5$ psia. After finding the equilibrium vapor compositions in the usual way, we can determine the liquid composition on the next tray by material balance. Below the feed use

$$x_{n+1} = (Bx_B + Vy_n)/(L + F)$$

The feed is introduced when $X_n > x_f$ following which use

$$x_{n+1} = (Bx_B + Vy_n - Fx_f)/L$$

where L, the liquid rate at the top of the column is given by V-D or 100 - 79.15 = 20.85 in this example. The stage calculations are listed below:

Stage	x	y	t°F	P psia
1	0.200	0.2822	365.1	17.50
2	0.268	0.4053	360.1	17.25
3	0.370	0.5902	350.1	17.00
4	0.523	0.8145	329.5	16.75
5	0.708	0.9527	300.7	16.50
6	0.823	0.9847	284.4	16.25
7	0.847	0.9889	280.2	16.00
	Plate 7 is the feed tray			
8	0.947	0.9978	269.3	15.75
9	0.990	0.9997	264.9	15.50
10	0.999	0.9999	263.2	15.25

The vapor leaving plate 10 exceeds the specification of $x_o = 0.9998$ and so plate 10 is the top tray.

Utility Requirements and Costs

The reboil steam used for the design was 1 mole steam per mole feed or 12 x 3,122 = 56.2×10^3 lb/hr.

If it is not possible to preheat the feed using waste heat from another process stream, extra steam will be needed. Butyl acetate has a specific heat of 0.46 Btu/16°F so this heat load is approximately

3,122 lb mole BA/hr x 116 lb BA/lb mole x 0.46 x (280-100) Btu/lb
= 30×10^6 Btu/hr

Thus the total heat load is about 86×10^6 Btu/hr and at a cost of \$2.50 per 10^6 Btu, the steam cost is \$1.80/10^3 gal wastewater treated. The total condenser heat load is the latent heat of the vapor plus the sensible heat to subcool the product. Butyl acetate has a latent heat of 133 Btu/lb so heat duty is:

$$3{,}122 \times 116 \text{ lb BA/hr} \times \left\{133 \text{ Btu/lb} + 0.79 \text{ lb product/lb feed} \times 0.46(263-100)\right\}$$

$$= 69.6 \times 10^6 \text{ Btu/hr}$$

Assuming a 25°F temperature rise and a cost of 12¢/10^3 gal circulated, cooling water costs are \$0.33/10^3 gal wastewater treated.

Equipment Sizes and Costs

The tower diameter can be found using the procedure given in Section 7. The liquid rate below the feed is 120.85 x 3,122/100 = 3,773 lb mole/hr. Using a molecular weight of 100 and a liquid density of 50 lb/ft^3 (6.0 lbs/gal), this becomes 3773 x 100/(6.0 x 60) = 1,048 gpm. The vapor density at 300°F and 16 psia is 0.196 lb/ft^3. The vapor rate is 3,122 lb moles/hr or 442.5 ft^3/s giving a vapor loading of 442.5 x $(0.196/50)^{1/2}$ = 27.7. A column diameter of about 11' 6" is required. The height of a 10 stage column with an assumed stage efficiency of 50%, 2 ft per plate and a 15 ft skirt, is about 60 ft. The volume of metal is 88,900 cubic inches or a metal mass of 25,200 lb. Assuming a cost factor of $10/lb and an installation factor of 3.75, the tower cost is $0.94 x 10^6. The reboiler condenser and reflux drum may be sized and costed as shown in Section 7 and will probably raise the cost to $1.06 x 10^6.

Phenol Still

The phenol still is designed to handle the full phenol (72 lb mole/hr) and water (450 lb mole/hr) load to the solvent still plus the phenol required for gas scrubbing in the solvent recovery section. We found in Section 3.2.2 that the optimum liquid-to-gas mole ratios in the water stripper and gas scrubber are about 18 and 0.05 respectively. As the water flow to the stripper is 10^6 lb/hr (5.56 x 10^4 lb mole/hr), the phenol rate to the scrubber is 5.56 x 10^4 x 0.05/18 = 150 lb moles/hr phenol. The total phenol rate to the phenol still is, therefore, (72 + 150) = 222 lb mole/hr and the total feed rate is 222 + 450 = 672 lb mole/hr. The water mole fraction in the feed is x_f = 450/672 = 0.67. Because this composition is similar to the rich phase concentration, it can feed into the top of the phenol tower. The rich phase from the decantor is recycled to the tower and the lean phase is recycled to the mixer-settlers. We have designed for a bottoms concentration of x_B = 0.0001 following the procedure given in Section 3.1. The stage calculations are listed below:

Stage	x	y	t°F	P psia
1	0.0001	0.0017	366.5	16.75
2	0.0013	0.0212	364.4	16.5
3	0.0156	0.2216	349.0	16.25
4	0.1636	0.8229	275.4	16.0
5	0.6077	0.9728	219.3	15.75

Plate 5 is the top and feed plate

Utility Requirements and Costs

The minimum vapor rate is 69.5 moles per 100 moles feed. We will use 90 moles per 100 moles feed or (90x661/100) = 595 lb mole/hr. The steam rate that will produce this vapor rate is equivalent to:

$$595 \text{ lb mole/hr} \times 94 \text{ lb/lb mole} \times 205 \text{ Btu/lb} = 11.5 \times 10^6 \text{ Btu/hr}$$

There is an additional heat load to heat the reflux from the decantor temperature (68°F) to the column temperature (224°F). The reflux rate is 21.9 moles/100 moles feed or 21.9 x 661/100) = 144.8 lb mole/hr and the reflux mixture has a specific heat of about 23 Btu/lb mole °F. The extra heat load is:

$$144.8 \text{ lb moles} \times 23 \text{ Btu/lb mole °F} \times (224-68)\text{°F} = 0.5 \times 10^6 \text{ Btu/hr}$$

The energy cost at $\$2.5/10^6$ Btu is 2.5 x (0.5 + 11.5) = \$30.1/hr or $\$0.25/10^3$ gals wastewater treated. The cooling load on the condenser is about equal to the total heat load of 12.0×10^6 Btu/hr, and cooling water costs at $12¢/10^3$ gals circulated, 25°F temperature rise, will be about $\$0.06/10^3$ gal wastewater treated.

Equipment Size and Costs

Using the methods described in Section 7, we obtain a liquid rate of 150 gpm and a vapor loading of 4.6 requiring a column diameter of 4 ft. With a plate efficiency of 50%,the 5 stage 10 plate column will have a height of 40 ft including a 15 ft skirt. The mass of metal is 3,700 lb, which at \$10/lb and an installation factor of 3.75 gives an installed cost of $\$0.14 \times 10^6$. The heat exchangers may be sized as suggested in Section 7 and this will increase the total cost to about $\$0.2 \times 10^6$.

Solvent Recovery (Figure 3-13)

Stripper. Butyl acetate has a solubility of 0.7 lb/100 lb water, so the concentration of the extracted wastewater fed to the stripper is

$$x_f = (0.7/116)/(100/18) = 0.0011$$

To recover 99.9% of this dissolved solvent, the bottoms concentration is:

$$x_1 = (1 - 0.999) \times 0.0011 = 1.1 \times 10^{-6}$$

A liquid to gas mole ratio (L/G) = 18 is used because we have shown that it is economical. We assume that the incoming gas is virtually solvent free, so $y_o = 0$. The stripper should be operated at low pressure; 18 psia (930.9 mm Hg) is specified for the bottom stage in this example. A pressure drop of 0.1 psi per stage is equivalent to 0.7" H_2O per foot of column height, based on a 50% stage efficiency and 2 ft of packing per actual stage (i.e. 4 ft per theoretical stage). This pressure drop is a conservative value for the packing described in Section 7.

Stage Calculations. The vapor concentration in equilibrium with the liquid is found first.

From Equation (31): $p_{BA} = 7.68.10^{6} \ x(1.1.10^{-6})^{2} + 19.44.10^{3} x1.1.10^{6}$
$= 0.0214$ mm Hg

From Equation (32): $y_1 = 0.0214\ (930.9 - 0.0214) = 22.99 \times 10^{-6}$

The liquid concentration on the next stage is:

From Equation (29): $x_2 = (22.99 \times 10^{-6} - 0)/18 + 1.1 \times 10^{-6} = 2.38 \times 10^{-6}$

The stage calculations continue until the liquid concentration equals or exceeds the feed concentration. This stage is then the top of the stripper.

Stage	x	y	P psia
1 Bottom	$1.1x10^{-6}$	$22.99x10^{-6}$	18.00
2	$2.38x10^{-6}$	$44.97x10^{-6}$	17.9
3	$3.88x10^{-6}$	$82.00x10^{-6}$	17.8
Etc.			
20	$5.16x10^{-4}$	$1.47x10^{-2}$	16.10
21	$8.18x10^{-4}$	$2.61x10^{-2}$	16.00
22 Top	$1.45x10^{-3}$	(Exceeds $x_f = 1.1x10^{-3}$)	

At 4 ft per theoretical stage, a packing height of 88 ft is required and the total column height will be about 100 ft.

Scrubber. If the gas leaving the stripper is in equilibrium with the feed water, it will have a vapor concentration calculated of $y_o = 0.041$ from Equations (31) and (32). We assume that the phenol scrubbing liquid is virtually solvent-free when it enters the scrubber, i.e. $x_N = 0$. In practice the phenol may be recycled with a bleed stream being taken to the phenol still. In this case $x_N \neq 0$ and must be calculated by material balance. If we use a liquid-to-gas mole ratio (L/G) = 0.05 and all the butyl acetate is absorbed into the phenol, then the phenol concentration leaving the scrubber is

$$x_1 = y_o/(L/G) = 0.041/0.05 = 0.82$$

If the total gas pressure drop in the scrubber system is 5 psi (2 psi for the stripper, 1 psi for the scrubber and 2 psi line losses), then the pressure at the bottom of the scrubber must be 15 + 5 = 20 psia (1,034 mm Hg).

Stage Calculations. The equilibrium vapor concentration is:

From Equation (33b): $p_{BA} = 34.5 \left\{0.82(1+0.82)\right\}^{1.76} = 8.480$ mm Hg

From Equation (32): $y_1 = 8.48/(1034 - 8.48) = 8.27 \times 10^{-3}$

The liquid concentration on the next stage is:

From Equation (29): $x_2 = (8.27\text{x}10^{-3} - 0.041)/0.05 + 0.82 = 0.165$

The stage calculations continue until the vapor is virtually free of solvent, about $y_M \simeq 10^{-8}$.

Stage	x	y	P psia
1 Bottom	0.820	$8.27\text{x}10^{-3}$	20.0
2	0.165	$1.31\text{x}10^{-3}$	19.9
3	$2.62\text{x}10^{-2}$	$2.37\text{x}10^{-4}$	19.8
Etc.			
8	$5.88\text{x}10^{-6}$	$5.60\text{x}10^{-8}$	19.3
9	$1.12\text{x}10^{-6}$	$1.07\text{x}10^{-8}$	19.2

At 4 ft per theoretical stage, a packing height of 36 ft is required and the total column height will be about 50 ft.

Utility Requirements and Costs. The major energy consumption is for circulating the gas. The horsepower required to adiabatically compress the gas from 15 to 20 psia is:

$$HP = 0.00078 \frac{WT}{Mne} \left[(P_2/P_1)^n - 1 \right]$$

where

W = gas mass flow rate

= $(10^6)/18)$ lb moles H_2O x $(1/18)$ lb moles gas/lb mole H_2O x 28 lb/lb mole gas

= 8.64×10^4 lb/hr

T = inlet temperature = 560°R

M = molecular weight of gas = 28 for nitrogen

n = 0.286 for adiabatic compression

e = overall efficiency = 0.7

The horsepower is 577 or 430 kw. If power costs 3¢/kw hr, then the compression costs are \$12.9/hr or $\$0.11/10^3$ gal wastewater treated. The installed cost of the compressor could amount to $\$10^6$.

Cooling water and liquid pumping costs may be determined following methods given in Section 7, but they are negligible relative to compression costs.

Equipment Costs. The diameter and cost of the packed columns are found in Section 7. The 100 ft stripper has a liquid rate of 10^6 lb/hr and a gas rate of 8.64×10^4 lb/hr and requires about a 7' diameter column costing \$190,000. The 60 ft scrubber has a liquid rate of 1.45×10^4 lb/hr and the same gas rate, requiring a 5'6" diameter column costing \$80,000. The installed cost of the two columns will be about $\$10^6$.

Summary of the Costs for Solvent Extraction

These costs, summarized in Table 3-2, provide an idea of the costs of solvent extraction in commercial sized coal conversion plants. They are useful for comparison with phenol removal by adsorption. We emphasize that approximate "rule of thumb" cost estimating has been used. In the preparation of a budget equipment costs supplied by vendors will be more accurate. Significant savings can be realized when integrating the plant into a coal conversion complex if energy conservation by heat interchange between process streams and waste heat boilers are used where feasible. Air coolers have higher capital costs than water cooled exchangers, but their overall costs may be lower for cooling at temperatures above 140°F and this should be checked.

Equipment costs in the table are the capital charges amortized at 15% per year and include an additional 4% maintenance charge. Labor and chemical costs are not included.

TABLE 3-2. APPROXIMATE COST OF PHENOL REMOVAL BY SOLVENT EXTRACTION[a]

	$\$/10^3$ gal[b]	% of Total
Extraction System		
Equipment	1.36	30
Solvent Regeneration		
Equipment: Solvent still	0.21	5
Phenol still	0.04	1
Utilities: Solvent still	2.13	46
Phenol still	0.32	7
Solvent Recovery		
Equipment (including compressor)	0.4	9
Utilities	0.11	2
	4.57	100

The costs may be partly offset by the market or energy value of the phenol that is recovered.

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a) These costs are to serve as a guide only. See text.
b) 8,000 stream hours/year.

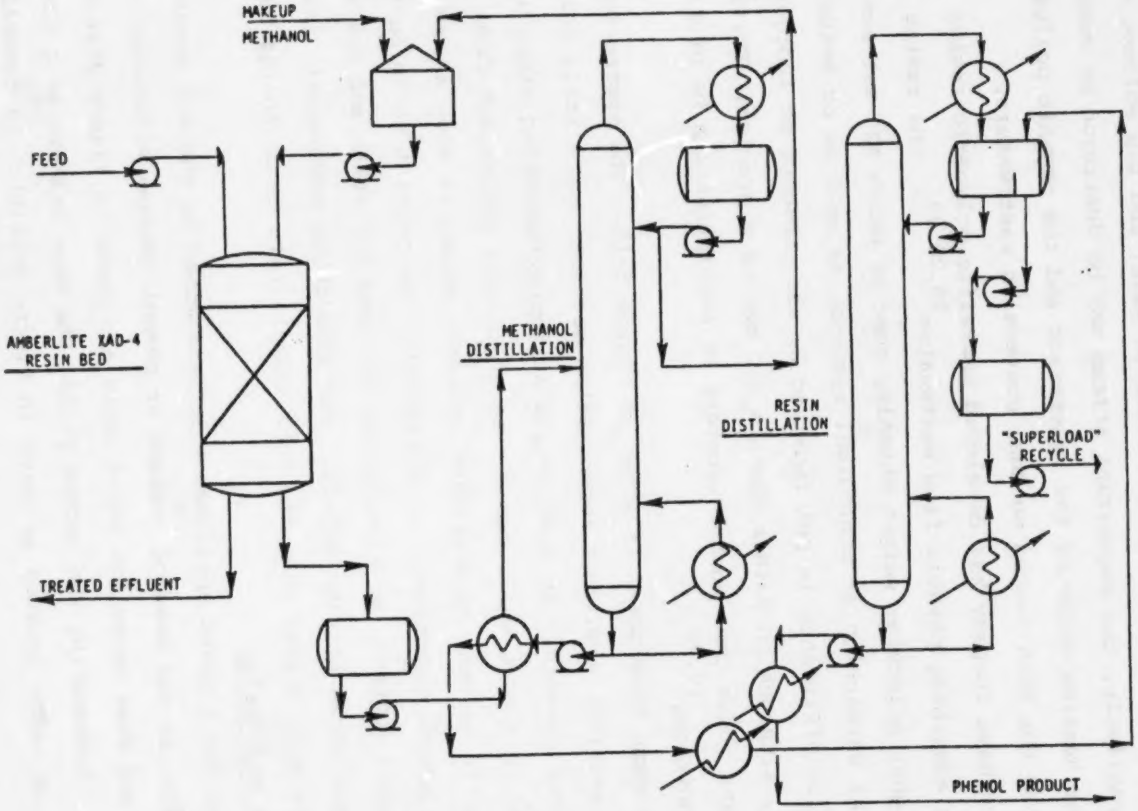
MAKEUP
METHANOL
FEED
AMBERLITE XAD-4
RESIN BED
TREATED EFFLUENT
METHANOL
DISTILLATION
RESIN
DISTILLATION
"SUPERLOAD"
RECYCLE
PHENOL PRODUCT

Figure 3-15. Phenol removal by resin adsorption.

3.3 Phenol Removal by Adsorption

Dissolved organics may be removed from aqueous streams by adsorption onto porous resins. The aqueous stream is passed through a bed of high surface area resin which adsorbs the organic pollutants and retains them by van der Waal forces. The binding energy is generally less than that for activated carbon adsorption and resin regeneration may be achieved easily by washing with solvent. The organic may be recovered for reuse or sale, and the solvent can be recycled. Alternatively, the regenerant stream may be destroyed by combustion, so recovering the heating value of the regenerant and the organic pollutant. This treatment has not been tested on coal conversion wastewaters.

The Rohm and Haas Company has developed Amberlite polymeric resins that are effective in adsorbing phenols from wastewater[19,20,23]. The resins reportedly[21] adsorb higher molecular weight phenols, some of which are not easily handled in solvent extraction or biological systems, as well as or better than C_6H_5OH. Adsorption efficiency is not impaired by the presence of inorganic salts or ammonia, although pH values above $\sim$ 8.2 may be a problem. Furthermore, cost estimates have shown that phenol recovery by adsorption can be profitable under certain conditions[19,20].

A typical process flow sheet is shown in Figure 3-15. The system consists of an adsorption section, a solvent regeneration section, and a still for drying the extracted phenols. In addition, a stripping/scrubbing step, not shown, may be used to remove small quantities of solvent regenerant from the treated water. While solvent regeneration consumes steam, it also allows for the recovery of a phenol byproduct. Alternatively, the solvent could be burnt along with its phenol content, so eliminating the need for steam and the two distillation columns shown in Figure 3-15. For this to be economical, solvent costs should not be much higher than the fuel (coal) costs on an energy basis.

3.3.1 Adsorption Bed Design

The bed volume for a given application is determined by the bed loading, lbs phenol/ft^3 resin, at the desired leakage or phenol removal efficiency. Bed loadings for Rohm and Haas Amberlite XAD-4 resin are shown in Figure 3-16(a) from Reference 22. Integrating the curves yields the mean leakage as a function of the volume of water treated as shown in Figure 3-16(b). In general, when designing adsorption beds, the greater the permissible leakage for a given flow, the greater the bed loading, and hence the longer the cycle or loading time. However, the mean leakage curves shown on Figure 3-16(b) are close to vertical and overall costs are not strongly dependent on the selected leakage. It is customary to design for zero or very low (1 mg/l) leakage. For low leakage:

$$\text{Bed loading (500 mg/l influent)} = 1.92 - 1.73\ q + 0.435\ q^2\ \text{lb/ft}^3 \tag{34}$$

where q = bed flow rate, gpm/ft^3 (∿ inverse residence time)

The bed loading increases with increasing effluent concentration as shown in Figure 3-17. Loadings at concentrations between 500 mg/l and 8,000 mg/l can be estimated by multiplying the value in Equation (34) by

$$\text{Bed loading factor} = 0.03\ C^{0.57} \tag{35}$$

where C = influent concentration, mg/l

Equations (34) and (35) are derived from available data for phenol and they may not be directly applicable to the range of phenols found in coal conversion condensates. They show that at a bed flow rate of 0.5 gpm/ft^3, the bed loading is 1.2 lb phenol/ft^3 resin at an influent concentration of 500 mg/l and 5.9 lb/ft^3 for an 8,000 mg/l feed. Bed costs would increase by a factor of ∿ 3 only for the 16 fold increase in concentration.

When the resin bed is loaded, it must be taken off line and regenerated. A second bed must then be available. Several beds are usually used in parallel so that only a small percentage of the total bed volume is off line at a time. Alternatively, it is possible to store the influent stream during the two-hour regeneration rather than provide additional bed volume. This is economical when the storage vessel costs less than the additional bed volume required for the regeneration step.

The fraction of the total bed volume that is loaded in two hours is:

$$v = (2/t_e)\ V \quad \text{ft}^3 \tag{36}$$

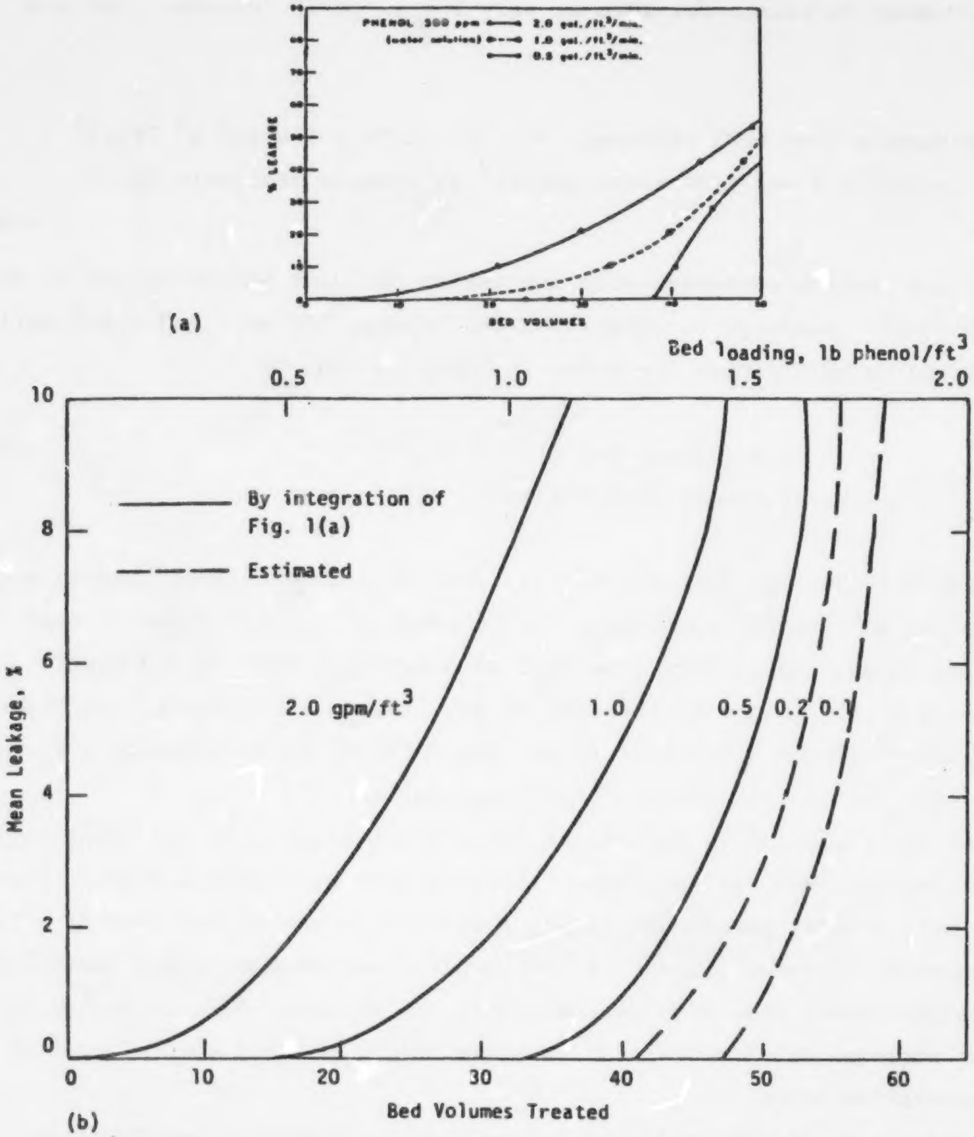

Figure 3-16. Effect of flow rate on resin capacity. (a) Instantaneous leakage, and (b) mean leakage, as a function of volume treated. Amberlite XAD-4 resin; 500 mg/l phenol in water stream.

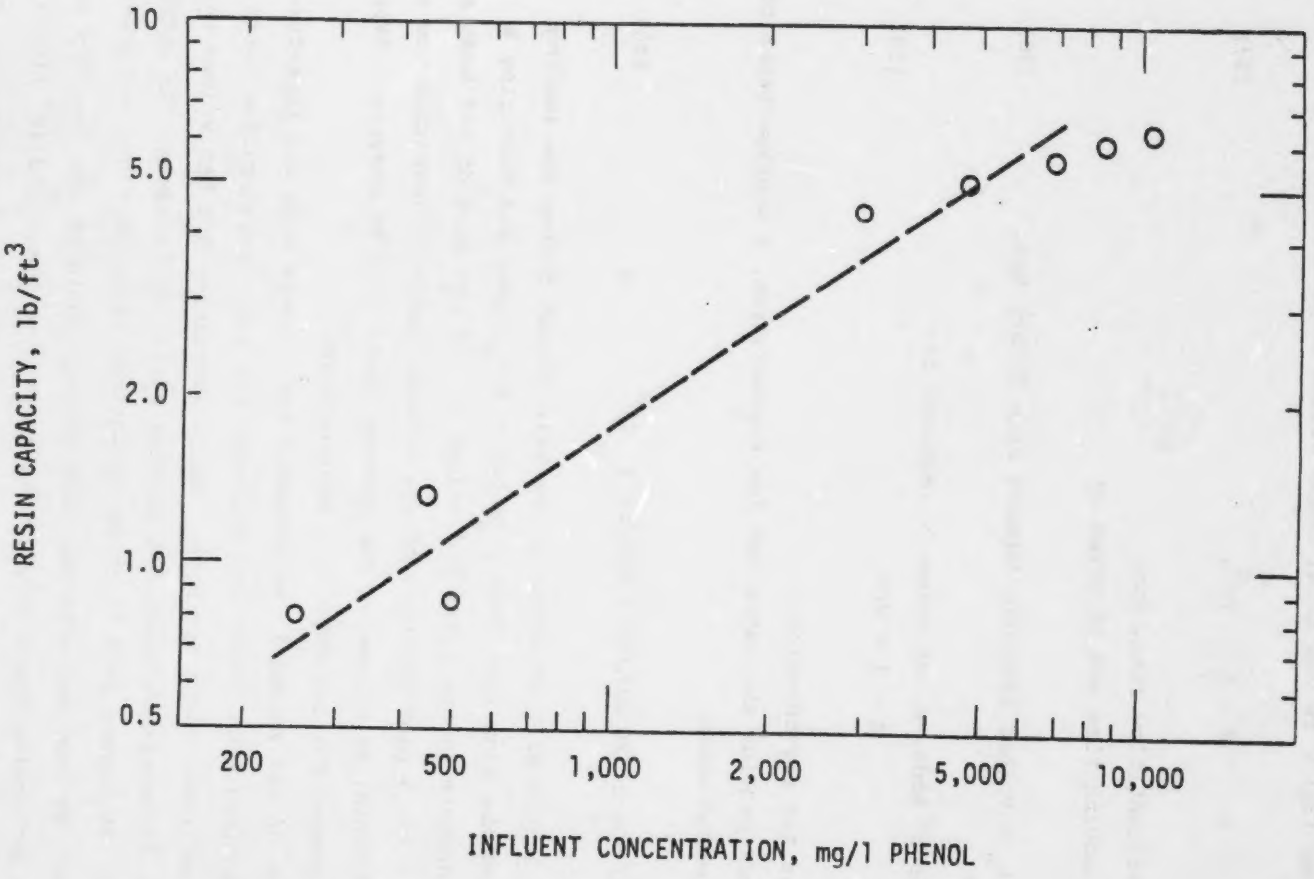

Figure 3-17. Effect of influent concentration on resin capacity. Based on data from References 20 and 21, flow rate = 0.5 gpm/ft^3 for zero or low leakage.

For continuity this must be the bed volume undergoing regeneration at any time. In Equation (36) V is the total resin volume required and is given by

$$V = \frac{Q}{q} \quad ft^3, \tag{37}$$

Q is the influent flow rate, gpm.

t_e is the loading time and is given by

$$t_e = V \text{ (bed loading)/(phenol rate lb/hr) hrs.} \tag{38}$$

The total number of beds, n, of volume v required is:

$$n = 1 + V/v \tag{39}$$

The extra bed is for regeneration.

If we do not provide the extra bed for regeneration, a storage basin of volume, s, is needed where:

$$S = Q \text{ gpm} \times 120 \text{ min}/(7.5 \text{ gal}/ft^3) \quad ft^3 \tag{40}$$

This volume of liquid will be added to the main stream during the loading cycle increasing the flow rate from Q to $Q(1 + 2/t_e)$ gpm, and requiring a proportional increase in the total bed volume V. If the cost of n-1 beds each of volume $v(1 + 2/t_e)$ plus the cost of the storage basin is less than the cost of n beds (and resin) of volume v, the storage route will be cheaper. Storage is generally cheaper for low feed rate applications.

The choice of bed volume is an economic one. Large beds and therefore high residence times mean higher bed loadings and lower regeneration costs. However, bed and resin costs are high. While decreasing the bed volume reduces capital costs, it increases steam and cooling water requirements. An optimum must be found. In Figure 3-18 is shown an optimum range of flows and phenol concentrations. We have included bed (and storage basin in the low flow case) capital costs and resins costs ($229/ft^3), as well as steam ($2/10^6 Btu) and cooling water (12¢/10^3 gal circulated) costs for methanol regeneration. A steam rate of double the theoretical minimum was used to allow for the need to

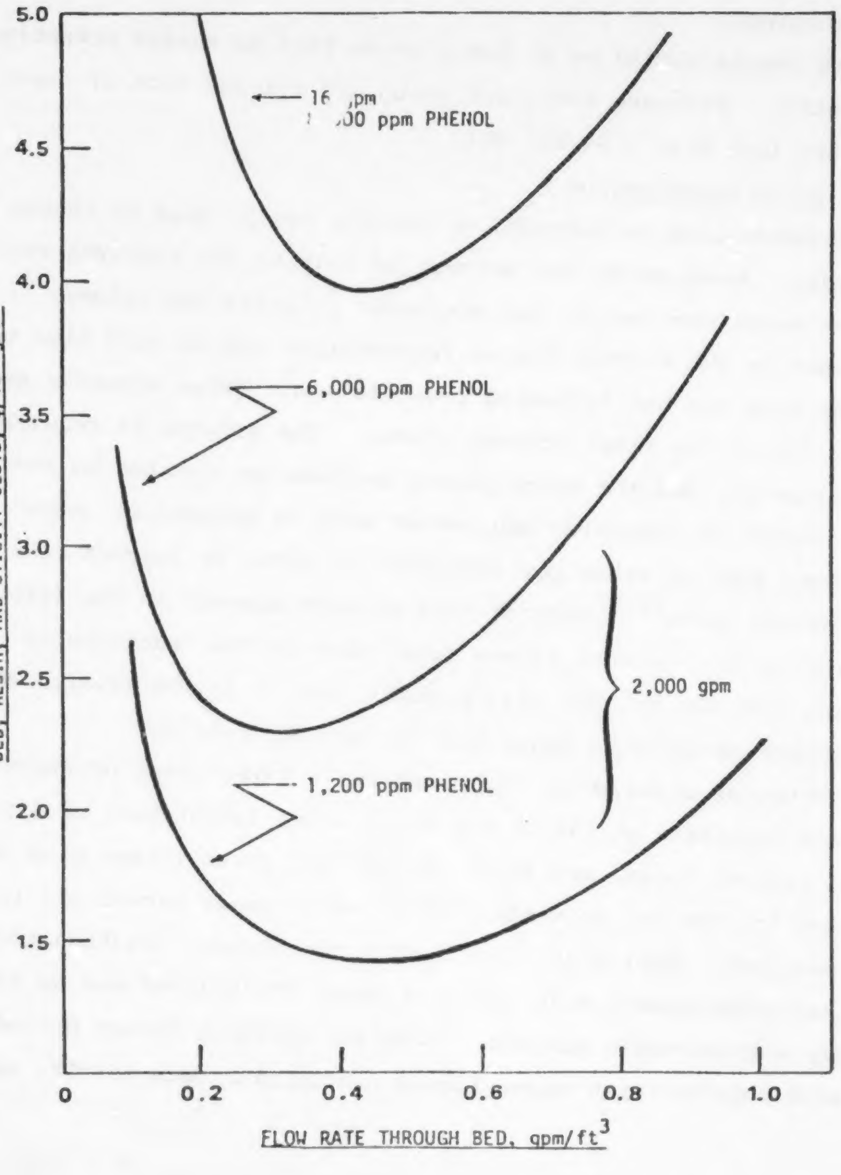

Figure 3-18. Bed flow rate (residence time) for minimum overall cost in phenol separation by resin adsorption.

reflux so as to achieve the desired separation. Cost of solvent losses, and capital requirements for solvent regeneration are not included in Figure 3-18, because they do not affect the flow rate value for minimum cost. The optimum flow rate falls in the range 0.3-0.5 gpm/ft^3, depending on phenol concentration and throughput.

Bed depths should be at least three feet to ensure effective resin utilization. Pressure drops are about 1/2 psi per foot of depth. Pumping costs are less than 0.5¢/10^3 gal.

3.3.2 Resin Regeneration

Solvents such as methanol or acetone may be used to absorb phenol from the resin. About three bed volumes of solvent are required with 1-1/2 bed volumes being used twice; the net usage is 1-1/2 bed volumes[21]. Water is entrained in the solvent during regeneration and is used also to displace solvent from the bed following regeneration. Water normally amounts to between 25% to 30% of the final solvent stream. The solvent is recovered by steam fractionation, and the water/phenol bottoms are treated to recover phenol.

Solvent is expensive and losses must be minimized. About 0.13 lb solvent per cubic foot of resin per regeneration cycle is leached from the bed during the loading cycle[21]. Most of this solvent appears in the first part of the loading cycle. Solvent losses occur also in the fractionator. Solvent leaving with the bottoms will probably end up in the treated effluent following the superloading cycle described in the next section.

Methanol costs about 7¢/lb and has a latent heat of 480 Btu/lb. Acetone is more expensive at 19¢/lb but has a lower latent heat of 225 Btu/lb. If total solvent losses are about 1%, overall costs (steam plus losses) are similar for the two solvents. If solvent losses exceed 1%, it is cheaper to use methanol. Typically, the feed to the solvent fractionator will have a solvent:water:phenol mole ratio of about 25:15:1 and may be treated as a binary solvent-water mixture. Standard textbook design procedures[24,36] may be used together with vapor-liquid equilibrium data for the selected solvent.

Vapor-liquid Equilibrium for Methanol-water System

Data at several pressures for both acetone and methanol are available in the literature[25,26]. The methanol data correlates well according to the Wilson equation[27], using Wilson coefficients[28]:

$$W_m = (v_w/v_m)/\exp(103.3/T°K) \tag{41}$$

and

$$W_w = (v_m/v_w)/\exp(242.7/T°K) \tag{42}$$

where the subscript m is for methanol, w for water. The molar volumes may be obtained for any temperature using:

$$v_m = 64.51 - 0.197T + 0.387 \times 10^{-3} T^2 \tag{43}$$

and

$$v_w = 22.89 - 0.036T + 0.686 \times 10^{-6} T^2 \tag{44}$$

In use, a temperature is assumed, the molar volumes and Wilson parameters calculated using the above equations, and the activity coefficients calculated using the Wilson equations given in Reference 27. If the sum of the vapor mole fractions is not unity, another temperature is selected and the calculations repeated. The procedure, which is similar to that for the van Laar equation described in Section 3.2, is illustrated in the example given at the end of this section.

The number of stages for a given separation is a function of the steam rate as shown in Figure 3-19 for production of a 99% pure methanol overhead. In practice the recovery efficiency must be high because any methanol in the bottoms will probably reach the main wastewater stream via the superload recycle. On the other hand, the overhead purity need not be high as a small amount of water in the methanol will not adversely affect resin regeneration. Minimum steam is about 65 lb/100 lb feed, or about 88 lb/100 lb methanol. The theoretical steam for evaporation is about 50 lb/100 lb methanol; the additional steam required for fractionation provides reflux. Lower reflux ratios can be used when a less pure overhead is acceptable. The actual steam rate/column size used will depend on their costs and the corresponding solvent loss. It turns out that minimum overall costs can be realized for high methanol recovery efficiencies (>99.9%) with tall columns at near minimum steam rate. At these

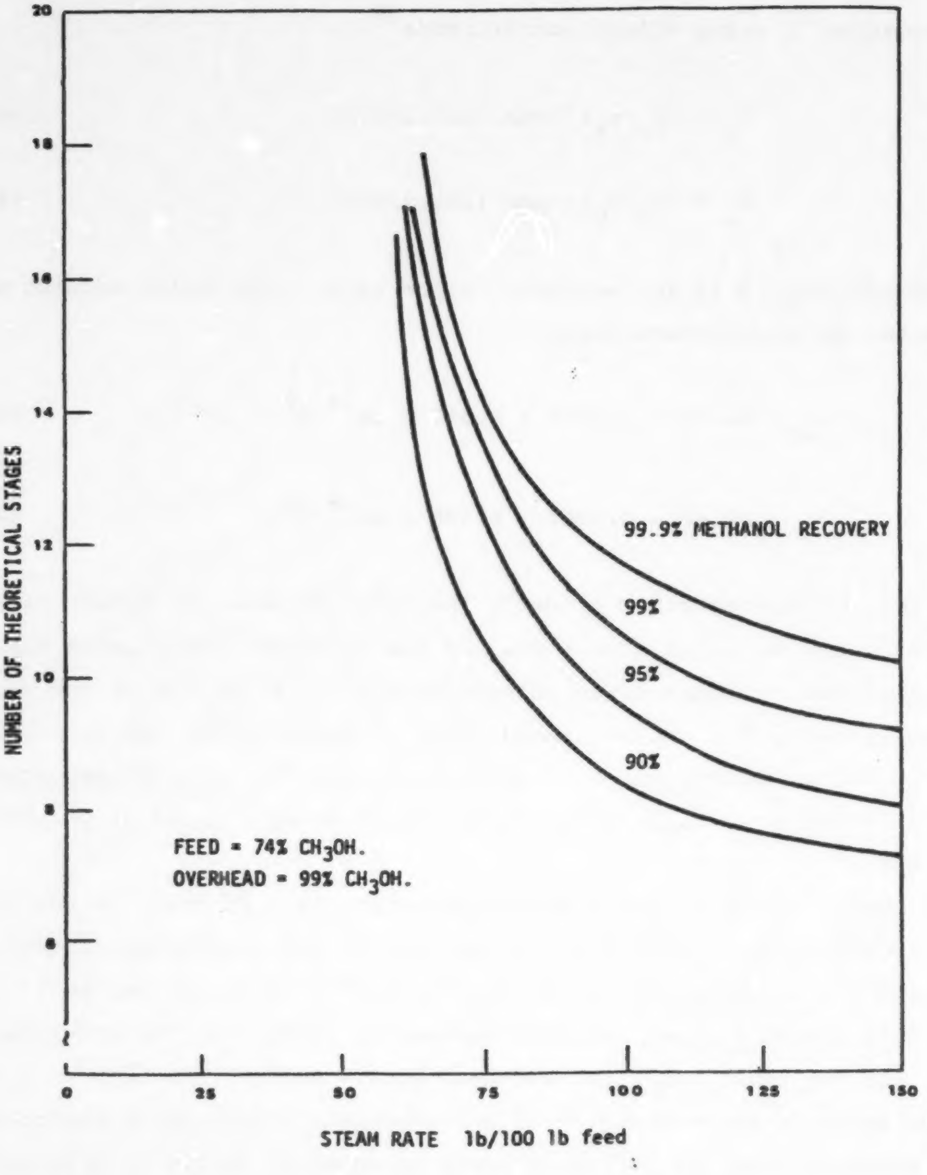

Figure 3-19. Theoretical stages and steam rate for methanol regeneration.

conditions the costs for regeneration including capital charges, steam and cooling water costs, as well as solvent losses amount to $1.30 per 1,000 gals. The solvent loss of about 0.1% is only in the solvent fractionator. Losses from mixing and leaching from the resin bed may be more significant. A total methanol loss of 1%[37] would add an additional $\$0.4/10^3$ gals to the operating costs.

Phenol Distillation

The bottoms from the solvent fractionation column contain about 30% phenol by mass. Removal of all of the phenol is expensive because the phenol-water system forms an azeotrope of 9.4% phenol by mass at atmospheric pressure, and 4.4% phenol at 5 psia. It is possible to break the azeotrope by a double distillation/decanting system[24], or by solvent extraction. If we choose atmospheric distillation, we must recycle a 9.4% phenol solution back to the adsorption bed. If we use the more expensive vacuum distillation route, we recycle 4.4% phenol; if we break the azeotrope, there is no need to recycle the water fraction of the regenerant stream. We have found that because the bed capacity increases with increasing influent concentration (Figure 3-17), recycling a concentrated stream of up to 10% phenol after blending it with the wastewater feed does not require additional bed capacity. In fact initial blending is not necessary. In the patented Rohm and Haas superloading process[23], the concentrated stream is passed directly through the resin bed at the end of the loading cycle, and then blended with the influent stream to another bed. Alternatively, the superloading water may be kept separate and used for solvent displacement. Since solvent not recovered in the fractionation tower will inevitably end up in the superloading water, use of the superloading water for solvent displacement might help reduce solvent losses.

The Rohm and Haas superloading scheme has been included in Figure 3-15. The solvent fractionator bottoms are first decanted since the phenol rich portion - about 30%-50% of the bottoms - is distilled in the phenol tower at atmospheric pressure. The overheads and the lean fraction from the decantor contain about 10% phenol. They are combined and used to superload the resin prior to regeneration.

The design of the phenol tower follows the method given in Section 3.1.

3.3.3 Example: Design of Resin Adsorption Plant

The plant will be based on the 2,000 gpm wastewater stream containing 6,000 mg/l phenol that as used for the solvent extraction example (Section 3.2.3).

1. Resin Bed Design

(a) Select optimum bed flow rate. In Figure 3-18 we indicate a rate of 0.3 gpm/ft^3; a value of 0.27 gpm/ft^3 gives a convenient loading time of 8 hrs and will therefore be used.

(b) Calculate bed loading. From Equations (34) and (35) with q = 0.27 and C = 6,000 mg/l:

$$\text{Bed loading} = 6.34 \text{ lb phenol/ft}^3 \text{ resin}$$

(c) Calculate bed volume. The total resin volume required is given by Equation (37):

$$V = 2{,}000 \text{ gpm}/(0.27 \text{ gpm/ft}^3) = 7{,}408 \text{ ft}^3$$

We will use 7,500 ft^3.

(d) Calculate loading time. The phenol rate to the resin beds is 2,000 gpm x 8.33 lb/gal x 6,000 x 10^{-6} lb/lb = 100 lb/min, or 6,000 lb/hr. Substituting in Equation (38) gives the loading time:

$$t_e = 7{,}500(\text{ft}^3) \times 6.34\ (\text{lb/ft}^3)/6{,}000\ (\text{lb/hr}) \simeq 8 \text{ hours}$$

(e) Number of beds and costs. From Equation (36) the bed volume undergoing regeneration at any time is:

$$V = (2/8) \times 7{,}500 = 1{,}875 \text{ ft}^3$$

The selected bed volume should either be 1,875 ft^3 or some whole number fraction of 1,875 ft^3. A volume of about 600 ft^3 is convenient; we will select one third of 1,875 ft^3 or 625 ft^3. From Equation (39) the total number of beds of this volume required is:

$$n = 3\ (1 + 7{,}500/1{,}875) = 15 \text{ beds}$$

of which three will be undergoing regeneration at any time. The cost of the skid mounted beds can be estimated from:

$$\text{Bed cost} = \$4{,}500\ (\text{Bed volume, ft}^3)^{0.55}$$

This equation gives a cost of $2.33 x 10^6 for the 15 beds. Resin cost, at $225/ft^3, adds an additional $2.11 x 10^6.

2. Methanol Distillation

(a) Feed composition to the methanol column. The volume of methanol used is 1.5 bed volumes per cycle, or 1.5 x 7,500 ft^3/8 hrs = 1,406 ft^3/hr. At a density of 49.3 lb/ft^3 this amounts to 69.3 x 10^3 lb/hr or 2.17 x 10^3 lb mole/hr. The water rate is taken to be 25% by volume of the methanol rate, that is 351.5 ft^3/hr, or 21.9 x 10^3 lb/hr, or 1.22 x 10^3 lb mole/hr. The phenol rate is the phenol input with the wastewater, plus the phenol recycled in the superload cycle. Assuming all the water entering the methanol tower is returned to the resin beds with the lean stream (9.4% phenol by mass) from the phenol tower decantor (see Figure 3-15), the phenol in the recycle stream is .094 x 21.9 x 10^3 = 2,060 lb/hr. The total phenol throughput is therefore 2,060 + 6,000 = 8,060 lb/hr or 85.7 lb mole/hr.

The total feed rate is 99.3 x 10^3 lb/hr or 3.48 x 10^3 lb mole/hr, and the mole fraction methanol in the feed is $x_f = 2.17/3.48 = 0.624$.

(b) Specify tower operating conditions. Any methanol not recovered in the methanol tower will be returned to the resin beds in the superload stream and may end up in the treated wastewater. Because there is no solvent recovery system proposed for the treated wastewater, a high methanol recovery of 99.9% is specified for the methanol distillation. However, the overhead need not be pure methanol and 95 mole % is probably adequate. We specify $x_D = 0.95$.

The minimum reflux rate is calculated from

$$R_{min} = (x_D - y_f)/(y_f - x_f)$$

and requires a knowledge of y_f, the vapor composition in equilibrium with the feed. Equilibrium vapor composition calculations proceed as in the phenol tower design example (Section 3.1.1), but here we use the Wilson equation parameters W_n and W_w given in Equations (41) and (42).

As before, temperatures are assumed and the resulting mole fraction water and methanol summed. If the sum exceeds 1.0, a lower temperature is selected;

if the sum is less than 1.0, the temperature is increased. At a temperature of 160.2°F (71.2°C, 344.1°K) and a total pressure of 15 psi (775 mm Hg), we get:

V_n, Molar volume of methanol (Eq 43) = 42.55 cm^3/g mole

V_w, Molar volume of water (Eq 44) = 18.63 cm^3/ g mole

W_n, Wilson coefficient for methanol (Eq 41) = 0.324

W_w, Wilson coefficient for water (Eq 43) = 1.129

Substituting in the Wilson equation given in Reference 27, we get the activity coefficient for methanol to be 1.065, and that for water to be 1.357. The vapor pressure of water is calculated from Equation (20) to be 246 mm Hg. The vapor pressure of methanol is given by

$$\log_{10} p^*_{\text{methanol}} = 7.879 - 1473/(230 + t°C)$$

which gives a value of 974 mm Hg. Substitution in the activity coefficient equations (Equation 14) gives

$$y_{\text{methanol}} = 1.065 \times 974 \times .624/775 = 0.835$$

$$y_{\text{water}} = 1.357 \times 246 \times (1 - .624)/775 = .162$$

The minimum reflux rates can now be calculated:

$$R_{\min} = (.95 - .835)/(.835 - .624) = 0.545$$

A value of R=1 will be used for this example.

(c) Calculate liquid and vapor flow rates. Based on 100 lb moles/hr feed, we get by material balance:

Product (distillate) rate:

$Dx_D = EFx_f$ or D = .995 x 100 x .624/.95 = 65.36 lb moles/hr

Bottoms rate:

B = 100 - D = 100 - 65.36 = 34.64 lb moles/hr

Vapor rate:

V = (R+1)D = 2 x 65.36 = 130.72 lb moles/hr

Liquid rate above feed:

L = V - D = 130.72 - 65.36 = 65.36 lb mole/hr

(d) Stagewise calculations. The stagewise calculations are made as for the butyl acetate distillation example in Section 3.2.3. The results are summarized below.

Stage	x	y	t°F	P psia
1 (bottom)	1.84×10^{-3}	1.46×10^{-2}	221	18
2	1.20×10^{-2}	8.71×10^{-2}	217	17.7
3	6.96×10^{-2}	0.342	202	17.4
4	0.272	0.636	181	17.1
5	0.507	0.780	170	16.8
6	0.620	0.834	165	16.5
7	0.663	0.853	163	16.2
The feed is introduced on Plate 7				
8	0.756	0.894	159	15.9
9	0.839	0.930	156	15.6
10	0.910	0.961	153	15.3

The vapor leaving plate 10 exceeds the product specification; plate 10 is therefore the top plate.

(e) Utility requirements and costs. The steam rate is calculated as in the example given in Section 3.2.3. A rate of 82×10^3 lb steam/hr is required for reboil and preheat. At $\$2.5/10^6$ Btu, the steam cost is $\$1.8/10^3$ gal wastewater treated. The cooling water required to condense the reflux and subcool the product is about 5,700 gpm, which at a cost of 12¢/10^3 gal cooling water circulated amounts to $\$0.34/10^3$ gal wastewater treated.

(f) Equipment size and cost. Using the equations given in Section 7 and following procedures outlined in previous examples, a tower diameter of 9 ft and a height of 60 ft is obtained at an installed cost of $\$642 \times 10^3$. Cost of the total condenser and reboiler will increase the total cost of the methanol regeneration to about $\$1.1 \times 10^6$.

3. Phenol Distillation

(a) Feed Composition. From the methanol tower calculations we have

Phenol rate = 8,060 lb/hr = 85.7 lb mole/hr
Water rate = 21,900 lb/hr = 1,220 lb mole/hr
Total feed = 29,960 lb/hr = 1,306 lb mole/hr

Water mole fraction in feed = 1,220/1,306 = 0.934

(b) Tower design. Design procedures for phenol distillation columns were presented in Section 3.1.1 and 3.2.2 and will not be repeated here. Five theoretical stages are required resulting in a 2'6" diameter 49 ft tall column with an installed cost of $\$90 \times 10^3$. Heat exchangers will boost the equipment cost to $\$170 \times 10^3$. Steam and cooling water costs are relatively small, amounting to $0.09 and $0.02 for each 1,000 gallons wastewater treated.

4. Summary of Costs for Resin Adsorption

The costs estimated in this example are summarized in Table 3-3 and are intended primarily for comparison with costs given in Table 3-2 for solvent extraction. They are not intended to represent an absolute cost for phenol removal. The tables show that the cost of phenol removal by both solvent extraction and resin adsorption fall in the range $4 to $5 per 1,000 gallons wastewater treated, the slightly higher cost for solvent extraction being attributable to the solvent recovery system.

A study of the distribution of costs for the two systems can indicate where improved design may lead to significant cost savings. For instance, both systems have high (∿50%) utility (energy) costs, and application of heat recovery techniques[40] or selection of solvent having lower latent heats should be considered.

The solvent extraction system has a high capital cost which can be reduced by decreasing the number of extraction stages. A reduction from six to two stages will reduce capital costs by 67% and it will now be economical to reduce the solvent/water flow ratio resulting in a proportional reduction in the utility costs for solvent regeneration. Of course, the penalty for the reduction in cost is a reduction in phenol removal efficiency as shown by Equation (25). However, the solvent extraction system may be followed by a resin adsorption system. Because the phenol load on the resin is now considerably reduced, regeneration frequency and consequently utility costs are reduced.

We have found that overall costs for a hybrid system may, for some wastewaters, be lower than the costs for either single system accomplishing the same job. Apart from economical advantages, the hybrid system may result in a cleaner effluent because pollutants not removed in the one system may be removed in the other. Further, a single solvent recovery system will serve to remove both solvents from the treated water. A small fractionation system may be added to separate the solvents and reduce the costs for solvent losses shown in Table 3-3.

TABLE 3-3. APPROXIMATE COST OF PHENOL REMOVAL BY RESIN ADSORPTION

	$\$/10^3$ gal		% of Total
Adsorption System			
Equipment	0.46		11
Resin, initial load	0.32		8
Resin, replacement (5 yr life)	0.43		10
Solvent Regeneration			
Equipment	0.22		5
Utilities	2.14		52
Methanol makeup (1% loss, 7¢/lb)	0.40		10
Phenol Distillation			
Equipment	0.03		1
Utilities	0.11	3	3
Total Cost	4.11		100

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4. AMMONIA SEPARATION AND RECOVERY

4.1 Introduction

Ammonia is formed in coal conversion reactors by the combination of nitrogen and hydrogen. Nitrogen is introduced to the reactors in combined form with the coal which may contain up to 2% nitrogen by mass. The proportion of this nitrogen that is converted to ammonia will depend on reactor conditions; up to 60% conversion has been reported for the Synthane process[17].

Large concentrations of atmospheric nitrogen are present in airblown gasifiers and may react

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \qquad (1)$$

The rate of reaction (1) is slow, but coal constituents could conceivably act as catalysts. Equilibrium is shifted to the right by decreasing temperature and increasing pressure.

Gaseous ammonia leaving the reactors is absorbed in the downstream quench step and removed with the dirty condensate waters. In low temperature gasifiers, e.g. Hygas, Lurgi, the resulting concentration of ammonia in the process condensate may range from 3,600 mg/l to 14,000 mg/l or more. These concentrations are considerably higher than those found in common wastewaters (for example, ammonia concentrations in raw sewage[1] are of the order of 35 mg/l and far in excess of those permissible for effluent discharge. High temperature gasifiers such as the Texaco and Koppers Totzek units are relatively clean burning and their process condensates may not need treatment for ammonia removal.

Since current trends are to reuse water and to minimize or possibly eliminate its discharge, we will briefly review the consequences of the presence of ammonia in the process condensate.

A major reuse proposed for process condensate is cooling. Ammonia in the cooling tower circuit provides nutrients for biological growth, leads to inactivation of zinc corrosion inhibitors, and consumes chlorine. It accelerates the corrosion of copper, so copper tubing should not be used. Ammonia is stripped from the water as it cascades down the cooling tower, and will therefore be present in the cooling tower plume. The threshold odor limit for ammonia has been stated to be 21.4 ppm[2]. If all the ammonia entering a cooling tower is stripped, then the ammonia concentration in the plume will be about one twenty-fifth that of the ammonia concentration in the makeup water (cooling tower operating with liquid to gas flow ratio of two to one, 2% of circulating water evaporated per cycle, about 10 cycles of concentration). The ammonia concentration in the makeup water must, therefore, be limited to below about 500 ppm to avoid exceeding the threshold concentration for odor. The ammonia concentration in the drift will be essentially the same as in the circulating water. Recommended values for ammonia concentration in the circulating cooling water of 75 ppm[3] and 10 ppm[12] have been reported. A full discussion of cooling water control is given in Section 6.

In some plants process condensate is recycled back to the process for slurrying the coal. Although a very clean water is probably not required, ammonia and other constituents may have to be removed to prevent their buildup in the recycle stream. As in the cooling water case, 100% ammonia removal is not necessary; it is sufficient merely to maintain an acceptable concentration level. This level must be determined.

Phenol is removed either by solvent extraction, resin adsorption, or by biological oxidation. Where the biological process is used, ammonia concentrations have to be reduced to below about 1,800 ppm[4] to prevent inhibition of the oxidation reactions. However, some ammonia is essential to provide nutrients; normally a phenol to N ratio of 14 to 1 is used.

In the case of solvent extraction, ammonia may or may not interfere, depending on the solvent used. On the other hand, if phenol is present in the ammonia stripper, some fraction of it will be stripped and may cause problems in downstream processing. For example, if the phenol is removed with the acid gases, it can accelerate deactivation of catalysts used in sulfur recovery, e.g. Claus processes. It is possible to hold down the phenols by refluxing the ammonia stripper, but this is expensive and would not normally be considered unless reflux was required for other reasons. Removal of phenol upstream of ammonia recovery may, therefore, be preferred. However, depending on its concentration, phenol removal by biological oxidation, which must follow the ammonia recovery step, may be cheaper. The final system choice will depend on the overall economics which must be determined for each specific case.

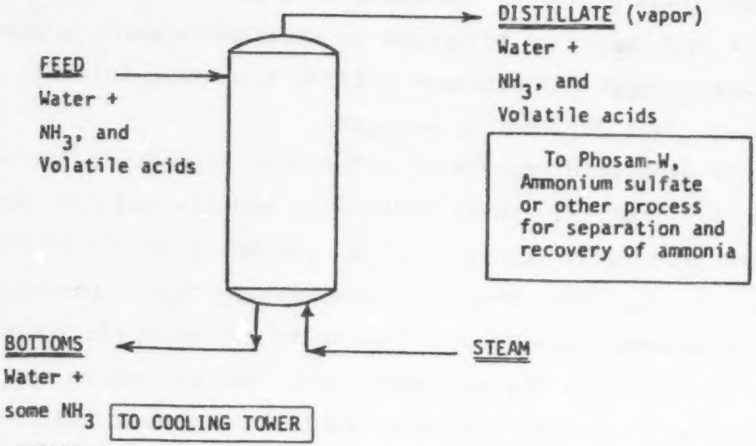
4.2 Ammonia Recovery Process

There are two major considerations. First, we do not wish to go from a water pollution to an air pollution or other disposal problem; second, ammonia removal is costly and we should try to recover our costs. Both factors dictate that we recover ammonia in a form suitable for sale, preferably as anhydrous ammonia or possibly as ammonium sulfate. In addition to ammonia, process condensates contain phenols and the volatile acid gases CO_2 and H_2S. While removal of ammonia from water by stripping is straightforward, separation of ammonia from carbon dioxide and hydrogen sulfide to obtain saleable ammonia is not straightforward; this defines the problem.

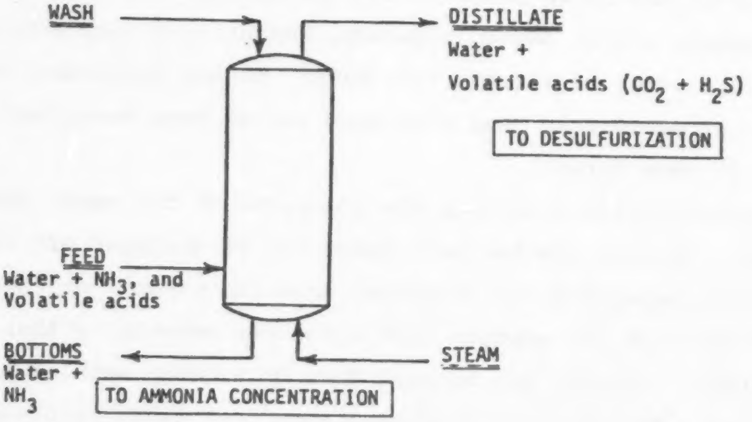
While there is published experience and design procedures for the treatment of sour waters[5], that is, waters containing ammonia and H_2S, we have found no published procedures relevant to the stripping of water containing ammonia, phenols, CO_2 and H_2S. There are proprietary design procedures for strippers treating aqueous feeds containing up to 30 component species[18] and they require the use of large digital computers. Our objective was to develop a relatively rapid calculational procedure suitable for desk top checking of demonstration plant designs. While we could not retain the versatility and detailed accuracy of the large programs, our procedure does meet the requirements of determining, within design accuracy, the utility requirements and stripper size for a range of process variables. To our knowledge, such procedures have not previously been published and we have described our design procedures here in some detail.

Two main possibilities exist for the stripping of the gases from the dirty condensate. Ammonia and the acid gases may be stripped off simultaneously with ammonia separated and recovered from the vapor. Or the acid gases may be stripped off with the ammonia held down; the ammonia is then concentrated in a separate stage. Ammonia may be held down by a water wash or a combination of wash and reflux. The stripper configurations that might arise are shown in Figure 4-1 (non-refluxed strippers) and Figure 4-2 (refluxed strippers). Reflux is used to concentrate the ammonia in the overheads when stripping a dilute (less than about 500 ppm NH_3) feed, or it may be used to hold back phenol, or in combination with a water wash to hold back ammonia.

It is useful to describe the design procedures for the stripping stage in the ammonia recovery schemes in the most general terms. In Section 4.3


DISTILLATE (vapor)
Water +
NH3, and
Volatile acids
To Phosam-W, Ammonium sulfate or other process for separation and recovery of ammonia
FEED
Water +
NH3, and
Volatile acids
BOTTOMS
Water +
some NH3
TO COOLING TOWER
STEAM

(A) STRIPPING


WASH
DISTILLATE
Water +
Volatile acids (CO2 + H2S)
TO DESULFURIZATION
FEED
Water + NH3, and
Volatile acids
BOTTOMS
Water +
NH3
TO AMMONIA CONCENTRATION
STEAM

(B) STRIPPING WITH WASH TO HOLD DOWN AMMONIA

Figure 4-1. First stage in ammonia recovery; stripping without reflux.

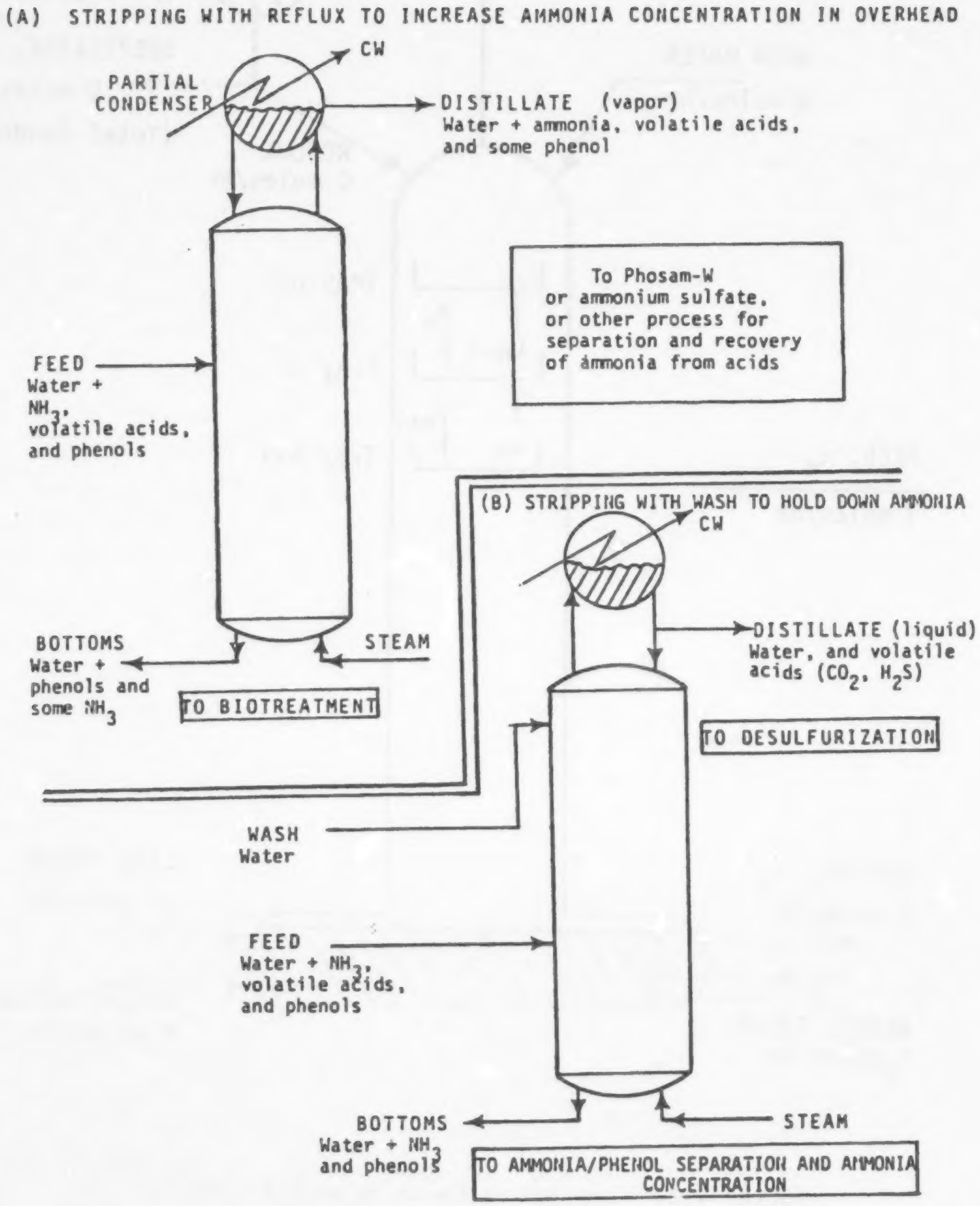

(A) STRIPPING WITH REFLUX TO INCREASE AMMONIA CONCENTRATION IN OVERHEAD
CW
PARTIAL CONDENSER
DISTILLATE (vapor)
Water + ammonia, volatile acids, and some phenol
To Phosam-W or ammonium sulfate, or other process for separation and recovery of ammonia from acids
FEED
Water + NH_3, volatile acids, and phenols
BOTTOMS
Water + phenols and some NH_3
STEAM
TO BIOTREATMENT
(B) STRIPPING WITH WASH TO HOLD DOWN AMMONIA
CW
DISTILLATE (liquid)
Water, and volatile acids (CO_2, H_2S)
TO DESULFURIZATION
WASH
Water
FEED
Water + NH_3, volatile acids, and phenols
BOTTOMS
Water + NH_3 and phenols
STEAM
TO AMMONIA/PHENOL SEPARATION AND AMMONIA CONCENTRATION

Figure 4-2. First stage in ammonia recovery; refluxed strippers.

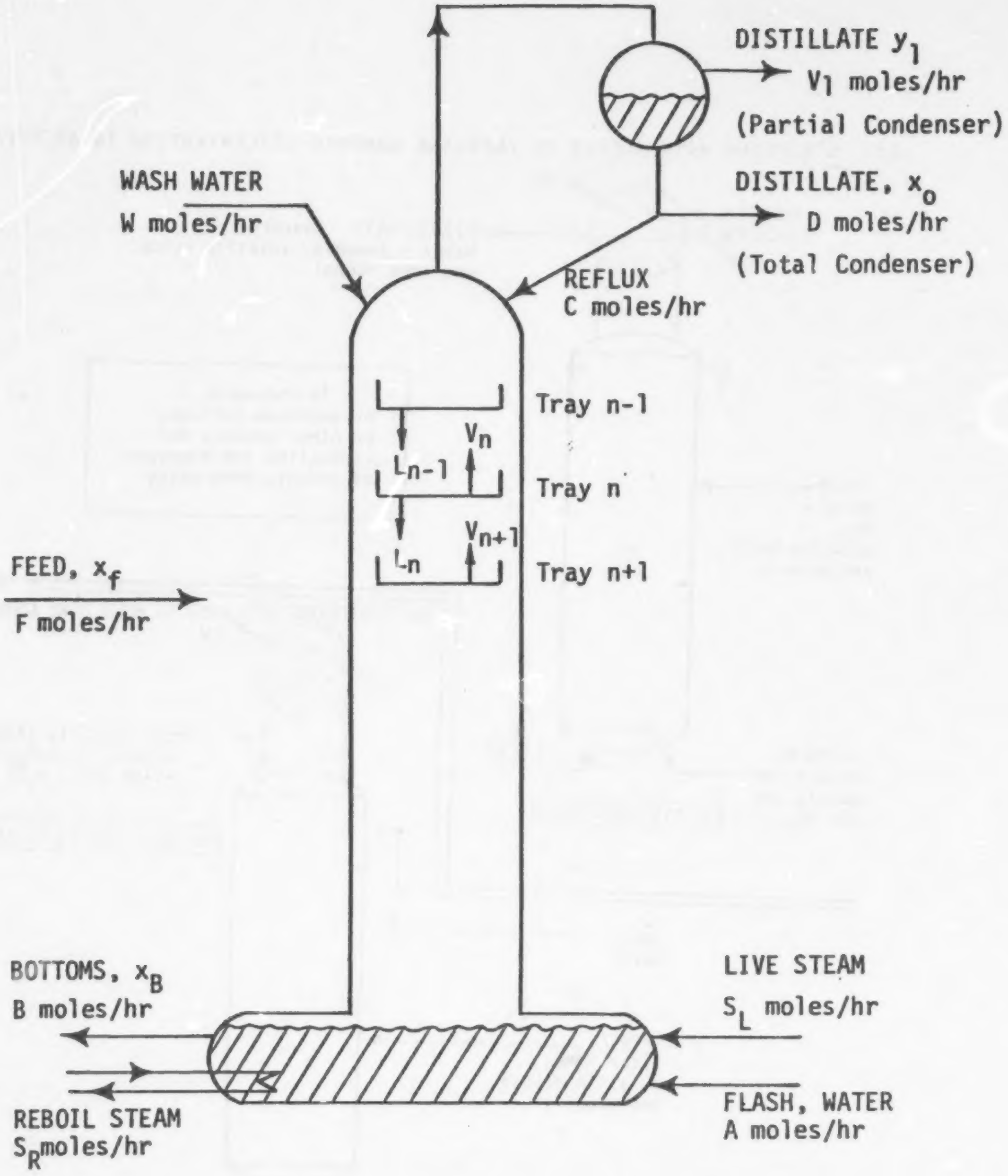

DISTILLATE y_1
V_1 moles/hr
(Partial Condenser)
WASH WATER
W moles/hr
DISTILLATE, x_o
D moles/hr
(Total Condenser)
REFLUX
C moles/hr
Tray n-1
V_n
L_{n-1}
Tray n
V_{n+1}
L_n
Tray n+1
FEED, x_f
F moles/hr
BOTTOMS, x_B
B moles/hr
LIVE STEAM
S_L moles/hr
REBOIL STEAM
S_R moles/hr
FLASH, WATER
A moles/hr

Figure 4-3. Stripping tower nomenclature.

a set of design equations incorporating all possible streams: feed, wash, reflux, hot water flash, etc. is developed. Those streams not required for a specific design are simply assigned zero values. Because of its generality, the procedure may be used for ammonia fractionation as well as stripping, and is applicable to the case where phenol is present and must be held down. The one limitation is that the aqueous ammonia product must not exceed 30% by mass. The production of more concentrated ammonia requires special treatment to account for departures from ideality with respect to both vapor-liquid equilibrium and heat effects. This is done in Section 4.4.

4.3 Stripping Tower Design

A typical stripping tower is shown in Figure 4-3. The condenser may be either a partial or total condenser, or may not be used. If a partial condenser is used, it is considered to be the first equilibrium stage in the column. In this case, and for the case of no condenser, material balance above the feed yields

$$W + V_{n+1} = V_1 + L_n \tag{2}$$

which, for any component becomes

$$y_{n+1} = \frac{V_1 y_1 + L_n x_n}{V_1 + L_n - W} \tag{3}$$

x and y are mole fractions; the nomenclature is given on Figure 4-3. Below the feed the equations become

$$W + V_{n+1} + F = V_1 + L_n \tag{4}$$

and

$$y_{n+1} = \frac{V_1 y_1 + L_n x_n - F x_f}{V_1 + L_n - W - F} \tag{5}$$

In the case of the total condenser, we must replace V_1 and y_1 by D and x_D respectively. However, the distillate or liquid concentration from the total condenser is identical to the vapor concentration entering the condenser which is y_1, the vapor concentration leaving the top plate.

In general the material balances become

$$W + V_{n+1} = X_1 + L_n - F \tag{6}$$

and

$$y_{n+1} = \frac{X_1 y_1 + L_n x_n - F x_f}{X_1 + L_n - W - F} \tag{7}$$

where

X_1 = D for total condenser

$X_1 = V_1$ for partial or no condenser

F = 0 above the feed plate.

We have chosen to treat the feed as a saturated liquid.

To being the calculations some conditions must be specified. We will specify the steam, flash and wash rates, the pressure at the top of the tower, and the type of condenser and reflux rates. If we are stripping, we must specify the amount of ammonia to be removed; if deacidifying, that is, removing only the acid gases, the amount of CO_2 to be removed must be specified.

We could not develop, from published vapor-liquid equilibrium data, a means of determining the complete overhead vapor composition from a knowledge of the pressure, temperature and the water vapor and ammonia (or CO_2) concentrations. It is therefore necessary to estimate removal efficiencies of three of the four components (the fourth component removal efficiency is specified) and to check the estimates by mass balance. Generally CO_2 is stripped in excess of 99% for 90% NH_3 removal. H_2S may or may not lead NH_3 stripping. If CO_2 is present, the H_2S is held down and under some conditions may concentrate in the tower until the CO_2 is stripped. Relative removal efficiencies are determined by their relative initial concentrations, temperature (pressure), steam rate, and whether or not reflux is used. The amount of water vapor leaving with the stripped gases is determined by heat balance.

It is assumed that the concentrations are everywhere sufficiently low that the enthalpies of the streams are those of pure water, and that the molal overflow rates based on the water component are equal. This assumption is probably not applicable to the vapor leaving the top tray, so in doing the heat balance only the water vapor component of this stream is considered.

The temperature everywhere is taken to be that equivalent to the water vapor pressure

$$t°F = \frac{7036.3}{14.49 - \ln P_v} - 384 \qquad (8)$$

where P_v is the vapor pressure of water, psia.

This equation, based on a Cox type plot, has an accuracy of better than 1/2% in the range $50 \leq t°F \leq 400$.

The overall balances for the tower, in the case of no condenser, are

$$\text{Material:} \quad F + S_L + A + W = B + V_1 \qquad (9)$$

Thermal:

$$FH_f + S_R(H_{v,B} - H_{\ell,B}) + S_L H_{v,B} + AH_{P,B} + WH_{\ell,1} = BH_{\ell B} + V_1 H_{v,1} y_{1,H_2O} \qquad (10)$$

where $H_{v,n}$ and $H_{\ell,n}$ are the molar vapor and liquid enthalpies of water at the conditions of stream n.

For the case of a partial condenser,

$$\text{Material:}\quad F + S_L + A + W = B + V_1 \tag{11}$$

$$\text{Thermal:}\quad FH_f + S_R(H_{v,B} - H_{\ell,B}) + S_L H_{v,B} + AH_{\ell,B} + WH_{\ell,1}$$

$$= BH_{\ell,B} + V_1 H_{v,1} y_{1,H_2O} + C(H_{v,1} - H_{\ell,1}) \tag{12}$$

For the case of a total condenser,

$$\text{Material:}\quad F + S_L + W + A = B + D \tag{13}$$

$$\text{Thermal:}\quad FH_f + S_R(H_{v,B}\ \ H_{P,B}) + S_L H_{v,B} + AH_{\ell,B} + WH_{\ell,1}$$

$$= BH_{\ell,B} + V_1 H_{v,1} y_{1,H_2O} - CH_{\ell,1} \tag{14}$$

For the general case, these equations may be written:

$$\text{Material:}\quad F + S_L + W + A = B + X_1 \tag{15}$$

$$\text{Thermal:}\quad V_1 = \frac{F(H_f - H_{\ell,B}) + (S_R + S_L)(H_{v,B} - H_{\ell,B}) + W(H_{\ell,1} - H_{\ell,B})}{y_{1,H_2O} H_{v,1} - H_{\ell,B} + X_2} \tag{16}$$

Where V_1 is the vapor from the top equilibrium stage,

$X_2 = R = 0$ for no condenser

$X_2 = R(H_{v,1} - H_{\ell,1})$ for partial condenser

$X_2 = \frac{R}{R+1}(H_{\ell,B} - H_{\ell,1})$ for total condenser

and R, the reflux ratio, is defined $R = \dfrac{C}{X_1}$ (17)

The feed must be introduced at the top if there is no condenser (R=0) and no wash (W=0). Otherwise, it may be introduced at a point where it improves the desired separation. For stripping, this will be where it increases the phenol to ammonia liquid concentration ratio; for deacidifying it will be where it increases the ammonia to CO_2 concentration ratio. Both the above feed and below feed material balance equations, Equations (6) and (7) must be used until the feed plate is found.

The feed enthalpy is that for the top plate when the feed is at the top (R and W = 0). Otherwise the feed enthalpy is not known in advance but may be estimated as being close to that of the top plate for stripping, or close to that of the reboiler if deacidifying.

The plate-by-plate calculations are begun by assuming a top temperature, calculating the water vapor concentration $y_{1,H_2O} = \frac{P_v}{P}$ using Equation (8), and then determining the top vapor rate using Equation (16). The temperature assumption is now checked by calculating the vapor composition from the top equilibrium stage using the specified removal efficiencies η_i:

$$y_{1,i} = \frac{\eta_i F x_{f,i}}{V_1} \tag{18}$$

The correct temperature is that for which $\Sigma y_i = 1$.

Once the top vapor is known, the equilibrium liquid composition is determined using the vapor-liquid equilibrium relationships presented in Section 4.3.1. The composition of the vapor from the next plate can then be calculated using Equation (7) for each component. The pressure on each successive plate is taken to increase by 0.5 psi, and the temperature of each plate is calculated using Equation (8). The calculations are repeated until the liquid composition satisfies one of the specified removal efficiencies. When stripping, the ammonia concentration is checked; when deacidifying, the CO_2 concentration is checked.

4.3.1 Vapor-liquid Equilibria for $H_2O - NH_3 - CO_2 - H_2S - C_6H_5OH$ System.

Van Krevelen et al[6] have published vapor-liquid equilibrium for the $H_2O - NH_3 - CO_2 - H_2S$ system; we have been unable to find data for this system in the presence of phenols. It is sometimes reported that phenol, being an acid, ties up the ammonia[19]. However, phenol has an ionization constant nearly three orders of magnitude less than that for H_2S[5], so we have made the assumption that the presence of phenol does not significantly affect van Krevelen's data.

Apart from phenol, there are eight species to consider: NH_3, NH_4^+, NH_2COO^-, CO_2, HCO_3^-, $CO_3^=$, H_2S and HS^-. The total ammonia concentration A, the total CO_2 concentration C, and the total H_2S concentration S, in moles/litre are given by:

$$A = (NH_3) + (NH_4^+) + (NH_2COO^-) \tag{19}$$

$$C = (CO_2) + (HCO_3^-) + (CO_3^=) + (NH_2COO^-) \tag{20}$$

$$S = (H_2S) + (HS^-) \tag{21}$$

Generally, (CO_2) and (H_2S) are negligible.

The relationships given by van Krevelen governing the concentration of the individual components are

The ionic balance:

$$(NH_4^+) = (HCO_3^-) + 2(CO_3^=) + (NH_2COO^-) + (HS^-) \tag{22}$$

The ionic equilibrium relationships:

$$K_1 = \frac{(HCO_3^-)(NH_4^+)}{(NH_3)\ p_{CO_2}} \tag{23}$$

$$K_2 = \frac{(NH_2COO^-)}{(NH_3)(HCO_3^-)} \tag{24}$$

$$K_3 = \frac{(NH_4^+)(CO_3^=)}{(NH_3)(HCO_3^-)} \qquad (25)$$

$$K_4 = \frac{(NH_4^+)(HS^-)}{(NH_3)\ p_{H_2S}} \qquad (26)$$

and Henry's law for ammonia:

$$p_{NH_3} = \frac{(NH_3)}{H_{NH_3}} \quad \text{mm Hg} \qquad (27)$$

The "constants" K_1 to K_4 and H_{NH_3} vary with system temperature and, in some cases, composition. Using data presented by van Krevelen, we obtain Antoine type correlations:

$$K_1 = \exp\left\{\frac{123935.}{t°F + 1605.5 - 8.64 \ln C} - 75.63\right\} \qquad (28)$$

$$K_2 = \exp\left\{\frac{4957.9}{t°F + 557.5} - 6.704\right\} \qquad (29)$$

$$K_3 = \exp\left\{\frac{10686.1}{t°F + 525.8} - 19.96\right\} \qquad (30)$$

$$K_4 = 10^{a_1 + 0.089S + a_2C} \qquad (31)$$

where $a_1 = - 0.168\ (t°C)^{0.627}$

and $a_2 = 0.0029\ (t°C)^{1.147}$

$$H_{NH_3} = H_0\ 10^{0.025(NH_3)} \qquad (32)$$

$$\text{where } H_o = \exp\left(\frac{4150}{T^oK} - 16.54\right) \tag{33}$$

K_1, K_4, H_{NH_3} as determined above are to be used with partial pressures expressed in mm Hg.

Van Krevelen developed a method for calculating the equilibrium vapor composition from a known liquid. In our work we start off with a specified vapor at the top of the stripping column and require the equilibrium liquid composition. This may be done as follows:

1) The free ammonia concentration is first determined from a knowledge of p_{NH_3} and Equations (27) and (32). Some iteration is required because the Henry coefficient is slightly dependent on (NH_3).

2) A value for (HCO_3^-) is then assumed and used to calculate (NH_2COO^-) from Equation (24).

3) C may now be calculated using Equation (20); as a first approximation $(CO_3^=)$ is taken to be zero. A better estimation of $(CO_3^=)$ is obtained using Equation (25) with Equation (30) after finding the (NH_4^+) concentration from Equation (23) and Equation (28).

4) Step 3 is repeated until the calculated $(CO_3^=)$ value stabilizes.

5a) (HS^-) is calculated from the ionic balance Equation (22) and used to calculate p_{H_2S} using Equation (26) and Equation (31). Steps 2 - 5 are repeated until the assumed (HCO_3^-) results in the known p_{H_2S}.

5b) In the case p_{H_2S} is zero, (HS^-) is zero and the assumed (HCO_3^-) value may be checked against one calculated from Equation (22).

The procedure is not suitable for systems containing H_2S in the absence of CO_2. In these cases use the following procedure:

1) The free ammonia concentration is determined.

2) A value of K_4 is calculated from Equation (31) with $C = 0$. As a first try, $S = 0$.

3) A better value for S is obtained using Equation (26). Note that for this system $(NH_4^+) = (HS^-) = S$.

4) Steps 2 and 3 are repeated until the value of S stabilizes. This fixes (NH_4^+) and hence A.

The above calculations are correct if fixed ammonia is not present; that is, if there is no mineral acidity and so no NH_4Cl or $(NH_4)_2\ SO_4$. If fixed ammonia is present, the calculations are approximately correct for that part of the ammonia which is free.

If phenol is present, its vapor pressure must be accounted for. Available data for phenol water systems (see Section 3) suggest that in the concentration range of interest the vapor-liquid equilibria for the phenol-water system is only slightly pressure dependent and may be adequately represented by:

$$y = 1.67\, x \qquad 15 \leq P \text{ psia} \leq 60 \qquad (34)$$

It is not known to what extent the presence of the ammonia and dissolved acid gases affect this equilibrium relationship. Equation (34) should nevertheless be used until information for the multicomponent system becomes available. Note that the condensates under consideration have phenol concentrations of less than 1% by mass so the phenol-water azeotrope (10% phenol by mass) is not a problem.

Example of Equilibrium Calculations

The liquid composition A = 1.189, C = 0.41 and S = 0.189 presented in Table 8 of van Krevelen's paper is used as a basis of the exemplary calculations. All concentrations are in g moles/l. Van Krevelen's procedure is used to calculate the equilibrium vapor composition:

1. Assume a value for the bicarbonate composition. As a first guess, use a value about 40% of the total CO_2 concentration; try $(HCO_3^-) = 0.17$.

2. Calculate (NH_3). From Equations (19), (20) and (21):

$$\begin{aligned}(NH_3) &= (HCO_3^-) + A - 2C - S\\ &= 0.17 + 1.189 - 2 \times 0.41 - 0.189\\ &= 0.35\end{aligned}$$

3. Calculate $(CO_3^=)$. Using Equations (20), (22), (25), and assuming $(CO_2) \simeq 0$ and that $(CO_3^=)$ is negligible relative to C:

$$(CO_3^=) = K_3\ (NH_3)(HCO_3^-)/(C + S)$$

From Equation (30) the value of K_3 at 20°C (68°F) is 0.140. Substituting:

$$(CO_3^=) = 0.140 \times 0.35 \times 0.17/(0.41 + 0.189)$$
$$= 0.014$$

4. Calculate (NH_4^+). From Equations (20) and (22):

$$(NH_4^+) = C + S + (CO_3^=)$$
$$= 0.41 + 0.189 + 0.014$$
$$= 0.613$$

5. Calculate $(NH_2\ COO^-)$ using Equations (24) and (29). From Equation (29) the value of the equilibrium constant is $K_2 = 3.395$. Substituting in Equation (24):

$$(NH_2\ COO^-) = K_2\ (NH_3)(HCO_3^-)$$
$$= 3.395 \times 0.35 \times 0.17$$
$$= 0.202$$

6. Check the ammonia balance using Equation (19):

$$A = (NH_3) + (NH_4^+) + (NH_2COO^-) \qquad (19)$$
$$= 0.35 + 0.613 + 0.202$$
$$= 1.165$$

But we know A = 1.187. Since the calculated ammonia balance is too low, we must increase the assumed bicarbonate concentration. Repeating the calculations:

1. Assume $(HCO_3^-) = 0.178$
2. $(NH_3) = 0.358$
3. $(CO_3^=) = 0.015$
4. $(NH_4^+) = 0.614$
5. $(NH_2COO^-) = 0.217$

The ammonia balance now gives

$$\begin{aligned} A &= 0.358 + 0.614 + 0.217 \\ &= 1.189 \end{aligned}$$

which coincides with the given liquid composition. The gas composition can now be calculated:

7. Determine the ammonia partial pressure. From Equation (33): H_o = 0.0929, and from Equation (32): H_{NH_3} = 0.0948. Substituting in Equation (27):

$$p_{NH_3} = 0.358/0.0948 = 3.776 \text{ mm Hg}$$

8. Determine the CO_2 partial pressure. From Equation (28): K_1 = 0.148. Substituting in Equation (23):

$$\begin{aligned} p_{CO_2} &= (HCO_3^-)(NH_4^+)/(K_1)(NH_3) \\ &= (0.178)(0.614)/(0.148)(0.358) \\ &= 2.066 \text{ mm Hg} \end{aligned}$$

9. Determine the H_2S partial pressure. From Equation (31): K_4 = 0.090. Substituting in Equation (26):

$$\begin{aligned} p_{H_2S} &= (NH_4^+)(S)/(K_4)(NH_3) \\ &= (0.614)(0.189)/(0.090)(0.358) \\ &= 3.602 \text{ mm Hg} \end{aligned}$$

As an exercise in determining equilibrium liquid compositions from a given vapor, the three partial pressures determined above will be used.

1. Calculate the free ammonia concentration. From Equation (33): H_o = 0.0929. Assuming $H_{NH_3} = H_o$, Equation (27) gives:

$$\begin{aligned} (NH_3) &= p_{NH_3} \times H_{NH_3} \\ &= 3.776 \times 0.0929 = 0.351 \end{aligned}$$

This value of (NH_3) is used in Equation (32) to calculate a more correct value of H_{NH_3} to get H_{NH_3} = 0.0948, which in turn gives (NH_3) = 0.358. Further iterations are not necessary.

2. Calculate (NH_2COO^-). A value of (HCO_3) is first assumed; we select $(HCO_3^-) = 0.178$. Substituting in Equation (24):

$$
\begin{aligned}
(NH_2COO^-) &= K_2\ (NH_3)(HCO_3^-) \\
&= 3.395 \times 0.358 \times 0.178 \\
&= 0.216
\end{aligned}
$$

3. Calculate the total CO_2 concentration.

$$
\begin{aligned}
C &= (CO_2) + (HCO_3^-) + (CO_3^{=}) + NH_2COO^-) \\
&= 0 + 0.178 + (CO_3^{=}) + 0.216 \\
\text{i.e.} \qquad C &= 0.394 + (CO_3^{=})
\end{aligned}
$$

To calculate $(CO_3^{=})$ use Equation (25), but must first estimate K and (NH_4^+). To calculate K from Equation (28) we require a value for C which is not yet accurately determined. As a first assumption use C = 0.394. This gives $K_1 = 0.146$ so that from Equation (23):

$$
\begin{aligned}
(NH_4^+) &= K_1\ (NH_3)\ P_{CO_2}/(HCO_3) \\
&= 0.146 \times 0.358 \times 2.066/0.178 \\
&= 0.605
\end{aligned}
$$

Substituting in Equation (25):

$$
\begin{aligned}
(CO_3^{=}) &= K_3\ (NH_3)(HCO_3)/(NH_4^+) \\
&= 0.140 \times 0.358 \times 0.178/0.605 \\
&= 0.015
\end{aligned}
$$

4. This value of $(CO_3^{=})$ is used to calculate a corrected value of C and the process is repeated until the calculated C concentration stabilizes. The first two iterations are:

Iteration	C	K_1	(NH_4^+)	$(CO_3^{=})$
1	0.394	0.146	0.605	0.015
2	0.409	0.148	0.613	0.015

The value of C stabilizes after only two iterations.

5. Calculate the (HS^-) concentration. From Equation (22):

$$\begin{aligned}(HS^-) &= (NH_4^+) - (HCO_3^-) - 2(CO_3^=) - (NH_2COO^-)\\ &= (0.613) - (0.178) - 2(0.015) - (0.216)\\ &= 0.189\end{aligned}$$

The partial pressure of H_2S is now calculated using Equation (26). From Equation (31) $K_4 = 0.090$ so:

$$\begin{aligned}P_{H_2S} &= (NH_4^+)(HS^-)/K_3(NH_3)\\ &= (0.613)(.189)/(0.090)(0.358)\\ &= 3.593\end{aligned}$$

The calculated H_2S partial pressure agrees closely with the given value of 3.602 so that the HCO_3^- concentration assumed in Step 2 must be correct. Had the calculated P_{H_2S} been too low, the assumed HCO_3^- concentration would have to be increased and the calculations repeated. The calculated liquid concentrations $A = (NH_3) + (NH_4^+) + (NH_2COO^-) = 1.187$, $C = 0.403$ and $S = 0.189$ agree closely with the liquid composition assumed originally.

4.3.2 Design Characteristics

The variation of stripper performance with steam rate, reflux, and wash is shown in Figures 4-4 through 4-6. The feed compositions used for the calculations are shown in Table 4-1. Composition "A" is typical of a Lurgi process condensate after solvent extraction and has a relatively high ammonia concentration; composition "B" is typical of a Hygas process condensate with a relatively low ammonia content but high phenol loading.

TABLE 4-1. COMPOSITION OF FEED TO STRIPPERS

Component	A. Typical Lurgi Condensate After Solvent Extraction		B. Typical Hygas Condensate	
	mg/l	Mole Fraction	mg/l	Mole Fraction
NH^3	17,000	0.0180	4,370	0.00466
CO_2	33,000	0.0135	7,600	0.00312
H_2S	100	0.000053	-	-
Phenols	300	0.000057	4,000	0.00076
H_2O		0.9684		0.9914

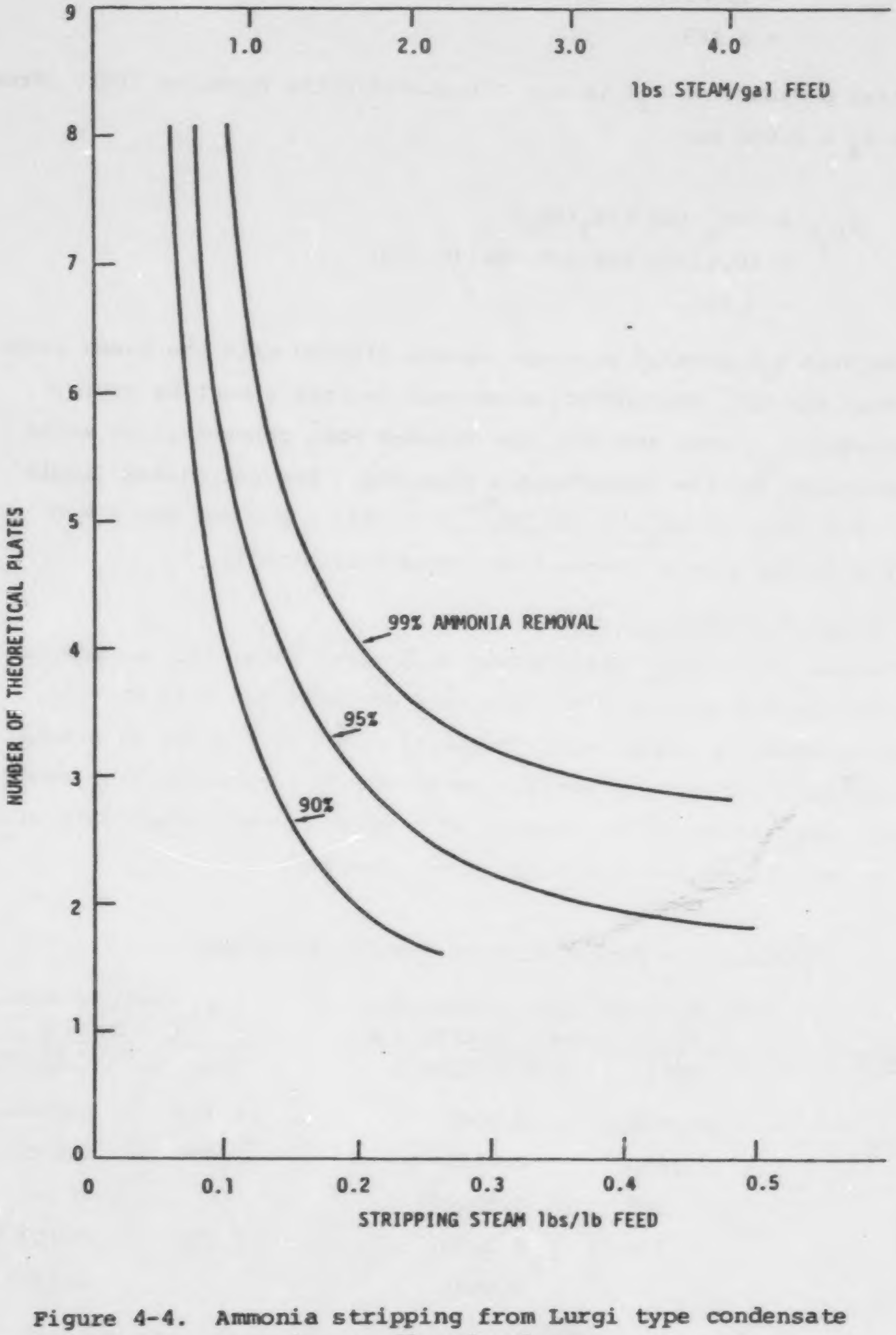


Figure 4-4. Ammonia stripping from Lurgi type condensate in unrefluxed columns.

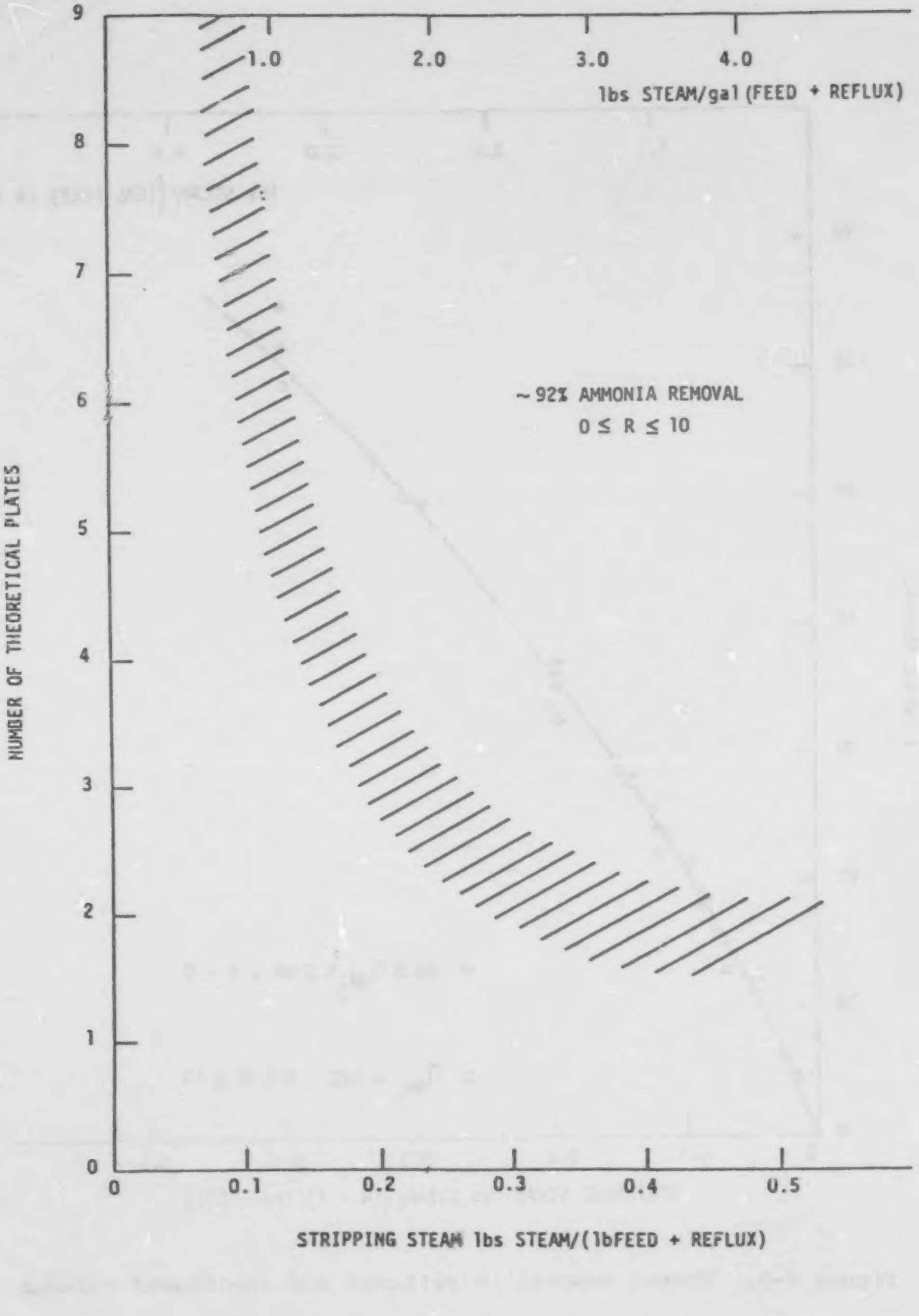


Figure 4-5. Ammonia stripping from Hygas type condensate in refluxed columns.

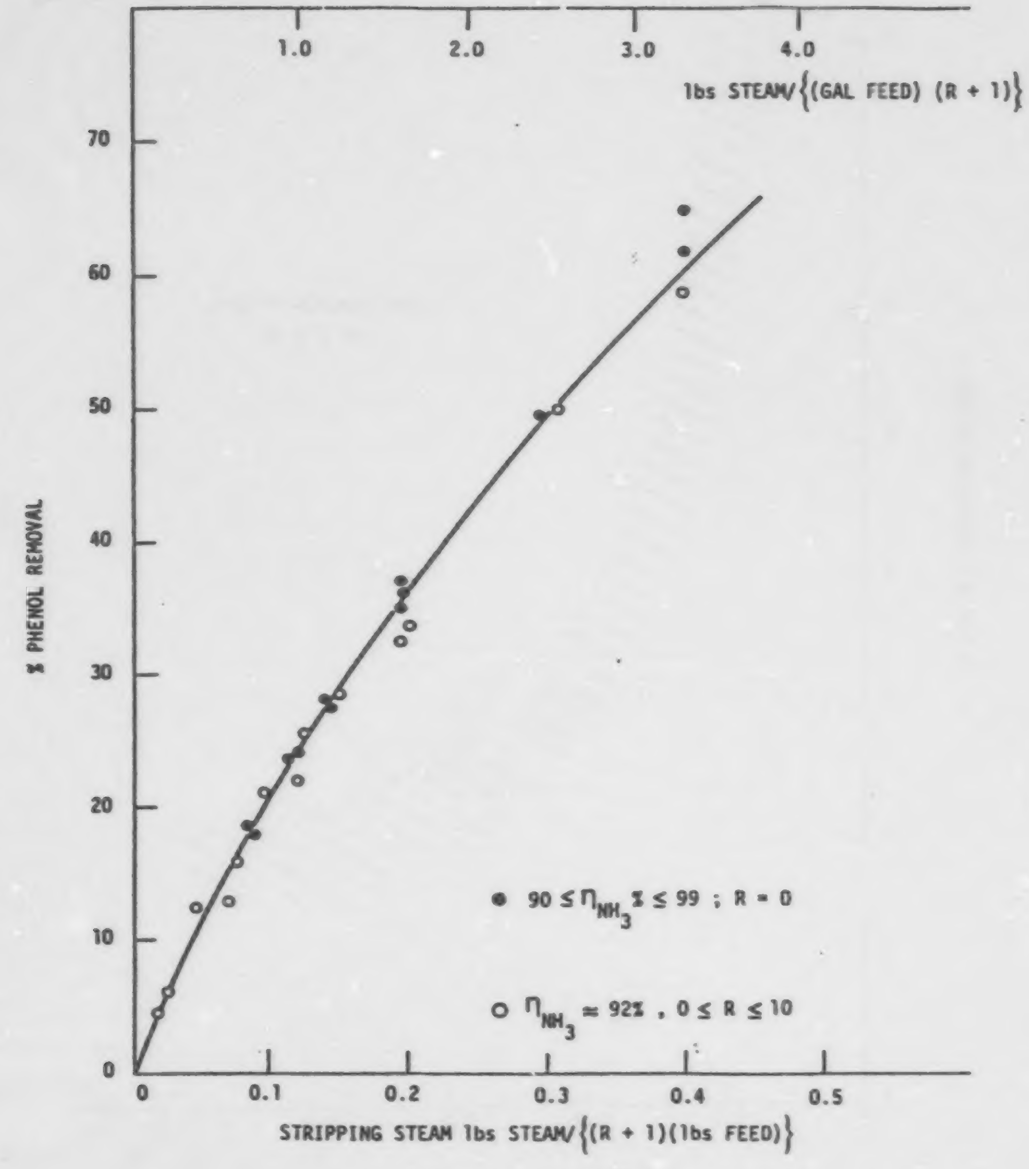


Figure 4-6. Phenol removal in refluxed and unrefluxed columns.

The relation between steam rate, number of theoretical plates and the stripping efficiency of ammonia from the Lurgi type feed water is shown in Figure 4-4 for columns operating at 25 psia. These data are for unrefluxed columns. The steam rate has to be approximately doubled to increase the ammonia removal from 90% to 99% for a fixed column height. Column heights cannot be significantly decreased by increasing the steam rate above ∿ 40 lbs. per 100 lbs feed (∿ 3 lbs steam/gallon feed); nor can significant steam savings be effected by increasing column heights above 8 to 10 theoretical stages.

Results for the Hygas type feed are shown in Figure 4-5 for 92% ammonia removal. The steam requirement increases with increasing reflux as do the cooling water requirements of the overhead partial condenser. Reflux, which results in increasing the ammonia concentration and decreasing the phenol concentration in the vapor, will be used only if it results in some downstream savings. For instance, USS Engineers and Consultants, Inc. (UEC) finds that refluxing is beneficial in the Phosam-W process (Section 4.5) if the ammonia concentration in the stripper feed is less than about 6,000 mg/l[10]. Refluxing increases the ammonia concentration and lowers the temperature in the ammonium phosphate absorber. This improves absorber performance resulting in both a decrease of absorber size and reduced steam requirements for absorbant regeneration.

The amount of phenol removed in the stripper is dependent on the steam rate and the amount of reflux as shown in Figure 4-6. Phenol may be held down by providing adequate reflux but this is expensive in steam. In the Phosam-W process some of the stripped phenol leaves the system with the absorber overheads while the remainder is carried over to the ammonia fractionator where it is removed by the addition of NaOH. UEC states[10] that as the phenol concentration in the absorber vapor increases, an increased in the NaOH consumption must be anticipated and this affects the operating cost of the plant slightly. If the phenol in the feed water exceeds 300 to 500 mg/l and if it is required to minimize NaOH consumption, reflux would be used but this results in an increase in both capital and operating costs. We do not expect reflux to be often used to hold down phenol.

A comparison was made between the theoretical results presented in this section and existing sour water (CO_2 free) stripper performance data given in References 5 and 11. The wide range in actual stripper performance makes direct comparison difficult. However, the smoothed characteristic curves presented in Reference 11 show that on increasing the stripping steam rate from 0.5 to 2 lbs steam per gallon, feed removal efficiencies for phenol increased from 20 to 48% and for ammonia from 80 to 99% in unrefluxed strippers. Our calculations for the same conditions yield phenol efficiencies from 15 to 44%, and virtually identical results for ammonia. Similar agreement was found for refluxed strippers.

4.3.3 Example: Design of an Ammonia Stripper

The number of theoretical stages required to strip 99% of the ammonia from the condensate A shown in Table 4-1 will be determined. A high steam rate of 20 lb steam per 100 lb feed will be used for this example and a column pressure of 25 psia at the top will be used.

1. Estimate overhead composition.

At this high ammonia removal efficiency, virtually all the CO_2 will be stripped. The H_2S concentration is relatively low, and in the presence of the large amount of CO_2 it may not be stripped as much as the ammonia. An indication of the phenol removal may be obtained from Figure 4-6. The following removal efficiencies are selected to begin the calculations:

Component	Removal Efficiency %
NH_3	99 (specified)
CO_2	100 (assumed)
H_2S	89 (assumed)
Phenol	36.8 (assumed)

2. Calculate top vapor rate.

A temperature is assumed at the top of the column which is slightly lower than the boiling point of pure water at the operating pressure; this is 232°F. At this temperature the molar enthalpies for water, obtained from steam tables, are:

Liquid water	200.25 x 18 = 3,605 Btu/lb mole
Saturated vapor	1157.7 x 18 = 20,837 Btu/lb mole

The vapor pressure of water at 232°F is 21.57 psia so the mole fraction water in the vapor at the top of the column is, approximately,

$$y_1 = 21.57/25.0 = 0.8628$$

According to Figure 4-4, about four theoretical stages will be required. The pressure at the reboiler (taking 0.5 psi per theoretical plate) will be 25 + (4-1) x 0.5 = 26.5 psia corresponding to a water boiling point of 243°F. At this temperature the water enthalpies are

Liquid water	211.4 x 18 = 3,805 Btu/lb mol
Saturated vapor	1161.5 x 18 = 20,907 Btu/lb mol

We now have sufficient information to use Equation 16, which may be written for this case:

$$V_1 = \frac{F(H_{\ell 1} - H_{P,B}) + S_R\,(H_{V,B} - H_{\ell,B})}{y_{1,H_2O}\,H_{V,1} - H_{\ell B}}$$

$$= \frac{100(3{,}605-3{,}805) + 20(20{,}907-3{,}805)}{0.8628 \times 20{,}837 - 3{,}805}$$

$$= 22.72$$

3. Calculate composition of vapor leaving top plate.

Applying Equation (18): $y = (\text{Efficiency }\%)\ x_f/V_1$:

NH_3: $y_1 = (99)(0.018)/22.72 = 0.0784$

CO_2: $y_1 = (100)(0.0135)/22.72 = 0.0594$

H_2S: $y_1 = (89)(0.000053)/22.7 = 0.000207$

phenol: $y_1 = (38.8)(0.000057)/22.7 = 0.000097$

Previously determined for water: $y = 0.828$

Total $\Sigma y = 1.001$

The mole fractions sum to 1.0 indicating that the assumption of 232°F at the top is correct. If the sum exceeds 1.0, a lower temperature must be tried; if the sum is less than 1.0, a higher temperature must be tried.

4. **Calculate the equilibrium liquid composition falling from the top plate.**

An example of the determination of the equilibrium NH_3, CO_2 and H_2S liquid concentrations was given in Section 4.3.1 and will not be repeated here. The phenol concentration in the liquid is estimated using Equation (34):

$$x = y/1.67 = 0.000097/1.67 = 0.000058$$

The complete composition of the liquid on plate 1 is:

Component	Mole Fraction in Liquid
NH_3	0.00729
CO_2	0.00107
H_2S	0.000017
Phenol	0.000058
Water (by difference)	0.99157
Sum	1.0

5. **Calculate the vapor rate from the second plate.**

A heat balance around each plate is required to exactly determine the flow rates from each plate. However, we are dealing with dilute mixtures and the liquid rate may be estimated with sufficient accuracy by assuming a constant molal overflow for water. This is equivalent to stating (Lx_{H_2O}) = constant. For the feed $Lx_{H_2O} = 100 \times 0.9684 = 96.84$. The liquid rate leaving plate 1 is

$$L_1 = 96.84/0.99157 = 97.66$$

Using Equation (6) the vapor rate from the plate below is calculated by material balance:

$$V_2 = V_1 + L_1 - F$$

$$= 22.72 + 97.66 - 100 = 20.38$$

6. Calculate composition of vapor leaving the second plate.

Equation (7) may be written

$$y_{n+1} = \frac{V_1 Y_1 + L_n x_n - F x_f}{V_1 + L_n - F}$$

NH$_3$: $$y_2 = \frac{(22.72)(0.0784) + (97.66)(0.00729) - (100)(.0180)}{22.72 + 97.66 - 100}$$

$$= 0.03401$$

CO$_2$: $y_2 = 0.00511$

H$_2$S: $y_2 = 0.000052$

phenol: $y_2 = 0.00010$

Water, by difference: $y_2 = 0.9607$

The temperature of this plate is assumed to be equivalent to the water vapor pressure. The total pressure on plate 2 is 25.5 psia. The partial pressure of water is 25.5 x 0.9607 = 24.50. The temperature is 239.3°F. The liquid composition is in equilibrium with the vapor at this temperature and the plate pressure of 25.5 psia is now calculated as in Step 4. Steps 4 to 6 are repeated until the required ammonia removal efficiency has been attained. The results are summarized in Table 4-2.

The table shows that the required ammonia removal efficiency of 99% is reached by plate 4 and that the CO_2, H_2S and phenol removal efficiencies correspond satisfactorily with the efficiencies originally assumed in Step 1. In cases where a poor initial estimate of a removal efficiency has been made, an improved value in between the assumed and calculated values should be selected and the stage calculations repeated.

TABLE 4-2. SUMMARY OF STAGE CALCULATIONS FOR AMMONIA STRIPPER

		Mole Fraction		Removal Efficiency*
Stage	Component	In Vapor	In Liquid	%
1	NH_3	0.0784	0.00729	68.7
	CO_2	0.0594	0.00107	93.9
	H_2S	0.000207	0.000017	75.2
	Phenol	0.000097	0.000058	21
	H_2O	0.8628	0.9916	-
2	NH_3	0.0340	0.00248	89.4
	CO_2	0.0051	0.000110	99.4
	H_2S	0.000052	0.000012	82.5
	Phenol	0.00010	0.000056	24
	H_2O	0.9607	0.9973	-
3	NH_3	0.0109	0.00076	96.7
	CO_2	0.00053	0.000009	99.9
	H_2S	0.000029	0.000012	82.5
	Phenol	0.000086	0.000052	29.5
	H_2O	0.9884	0.9992	-
4	NH_3	0.00289	0.000202	99.1
	CO_2	0.000047	∿ 0	∿ 100
	H_2S	0.000029	0.000008	88.3
	Phenol	0.000072	0.000043	41.4
	H_2O	0.9970	0.9997	-

---

*Calculated using Efficiency = $1 - (Bx_n)/(Fx_f)$ with $B = 100 - V_1$, $100 - 22.72 = 77.28$

4.4 Concentrated Ammonia Fractionation

There are only two components: ammonia and water. However, elementary textbook calculations are inadequate because the modified Henry law for ammonia as used by van Krevelen[6] at low concentrations is not valid above a vapor concentration of about 30% by mass and we wish to produce 99.9% ammonia. No suitable correlations were found in the literature. In addition, the molal heat of vaporization of ammonia is approximately half that of water and ammonia has a significant heat of solution. These heat effects could be neglected in the dilute system but must be accounted for in concentrated solutions by doing an enthalpy balance around each plate.

In making concentrated ammonia, we will generally require a liquid product and so the tower will be fitted with a total condenser. A typical tower is shown in Figure 4.7. A material balance for tray n is;

$$V_{n+1} = L_n + D - F \tag{35}$$

which for the ammonia component becomes

$$V_{n+1}\, y_{n+1} = L_n x_n + Dx_D - Fx_f \tag{36}$$

Equations (35) and (36) yield:

$$L_n = \frac{D(x_D - y_{n+1}) + F(y_{n+1} - x_f)}{y_{n+1} - x_n} \tag{37}$$

The enthalpy balance for plate n is:

$$V_{n+1}\, H_{v,n+1} + L_o H_{\ell,1} = V_1\, H_{v,1} + L_n\, H_{\ell,n} - FH_{\ell,f} \tag{38}$$

On substituting $R = \frac{L_o}{D}$, $V_1 = L_o + D = D(R+1)$, and Equation (35) into the enthalpy balance:

$$L_n = \frac{D\left\{(R+1)H_{v,1} - RH_{\ell,1} - H_{v,n+1}\right\} + F(H_{v,n+1} - H_{\ell,f})}{H_{v,n+1} - H_{\ell,n}} \tag{39}$$

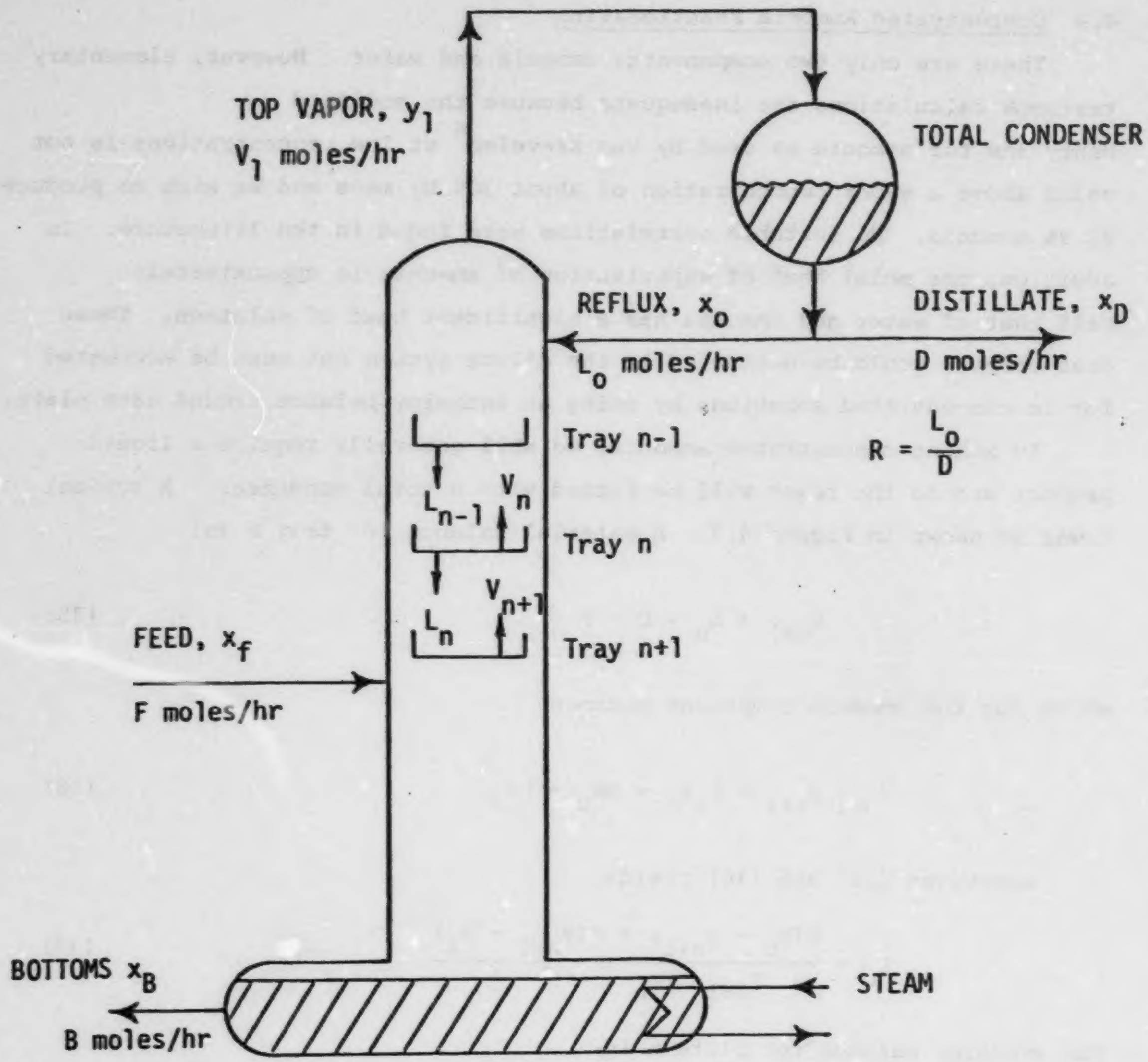

TOP VAPOR, y_1
V_1 moles/hr
TOTAL CONDENSER
REFLUX, x_o
L_o moles/hr
DISTILLATE, x_D
D moles/hr
$R = \frac{L_o}{D}$
Tray n-1
L_{n-1}
V_n
Tray n
L_n
V_{n+1}
Tray n+1
FEED, x_f
F moles/hr
BOTTOMS x_B
B moles/hr
STEAM

Figure 4-7. Concentrated ammonia still.

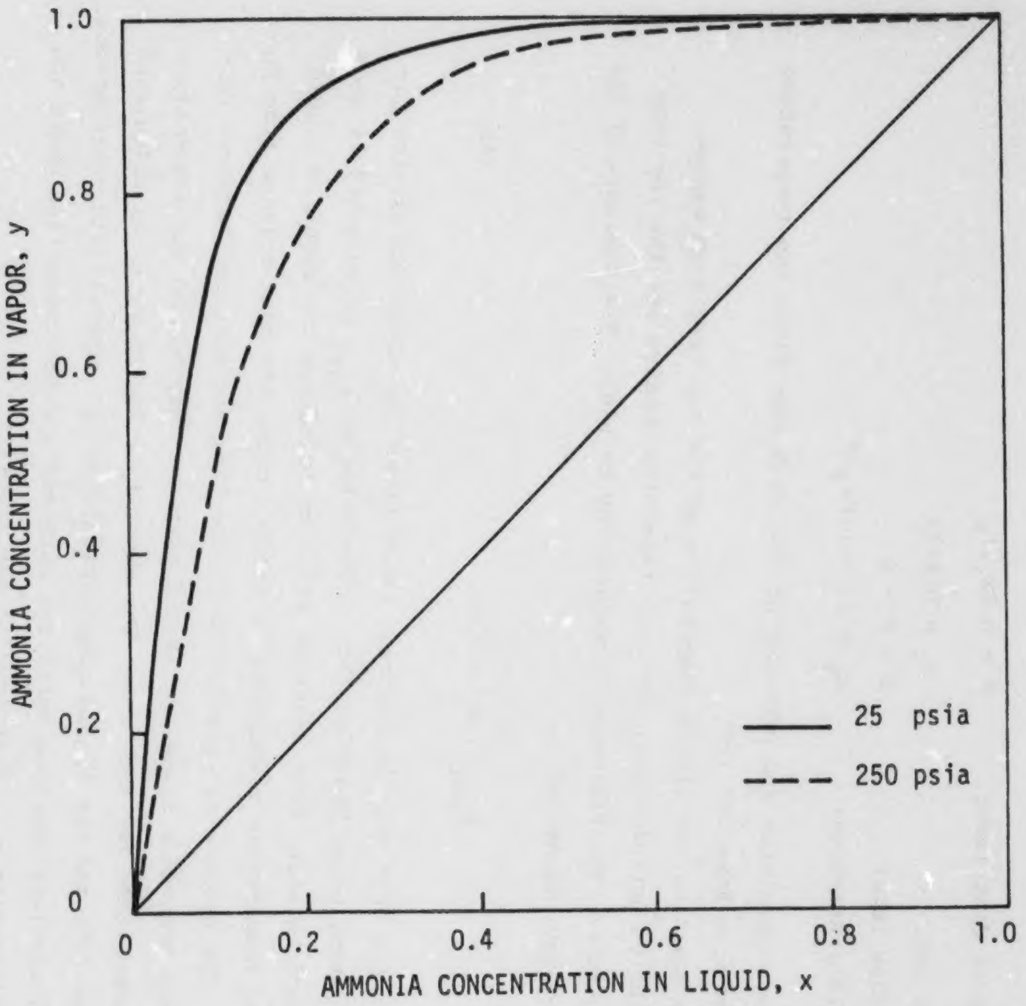


Figure 4-8. Dependence of ammonia vapor-liquid equilibrium on operating pressure.

The value of F is zero when Equations (35) to (39) are used above the feed. The feed tray is that for which $x_n \leq x_f$.

The tray-by-tray calculations proceed as follows: Specify the distillate composition x_D, the condenser pressure P, the reflux ratio R, and the ammonia removal efficiency η. For the total condenser, $x_D = y_1 = x_0$. Calculate:

flow rate of distillate: $D = \eta F x_f / x_D$

top vapor rate: $V_1 = D(R+1)$

bottoms flow rate: $B = F - D$

bottoms concentration: $x_B = (1 - \eta) F x_f / B$

Specifying the composition and pressure of the condenser fixes the temperature which is found from Equation (46).

After determining the liquid composition of the top tray from vapor-liquid equilibrium correlations, the only remaining unknown for the top tray is the liquid rate. The following procedure may be used. The pressure of the next tray, n+1 say, is set at

$$P_{n+1} = P_n + 0.5 \tag{40}$$

A temperature for this tray is assumed, which fixes the vapor composition for the binary system, using Equation (46). The value of y_{n+1} so obtained is used in the material balance, from Equation (37), to calculate the required liquid rate L_n. The temperature assumption is checked using the heat balance from Equation (39). The process is repeated until the heat and material balances correspond. This procedure fixes the liquid rate for tray n, and the temperature and vapor composition for tray n+1. The vapor rate for tray n+1 is calculated from Equation (35) and the liquid composition from the vapor-liquid correlations.

The calculations continue until the obtained liquid composition meets the bottoms specification x_B. This tray is the reboiler.

4.4.1. Vapor-liquid Equilibria for the Ammonia-water System

There are two degrees of freedom for the binary system. The vapor composition is fixed and may be calculated once the liquid composition and pressure (or temperature) is stated:

$$y = f(x, P) \tag{41}$$

This is the usual way of presenting vapor-liquid equilibria. The form of relationship for the ammonia-water system is shown in Figure 4-8.

For our calculations it was useful to have a slightly different relationship:

$$y = f(t, P) \tag{42}$$

$$x = f(t, P) \tag{43}$$

A knowledge of pressure and temperature can be used to calculate both liquid and vapor composition. Alternatively, a knowledge of pressure and any one composition can be used to determine the temperature and the other composition. Published[8,9] vapor-liquid equilibrium data for the ammonia-water system were used to obtain the correlations.

(a) Vapor composition

If P_v is the vapor pressure of pure water, P is the total pressure and x and y are the mole fractions ammonia in the liquid and vapor phase respectively, then Raoult's law may be written:

$$(1-y) = P_v(1-x)/P \tag{44}$$

Since the ratio $\frac{P_v}{P}$ is unique for any temperature and pressure, both the liquid and vapor compositions must be a unique function of this ratio. The vapor composition may be represented by;

$$(1-y) = f(P_v/P) \tag{45}$$

where the function f includes deviations from Raoult's law. Figure 4-9 is a plot of (1-y) vs. P_v/P. Over most of the concentration range for which data are available, a least squares fit of the variables used in Equation (45) gave:

$$(1 - y) = 1.03\ (P_v/P)^{1.27}, \quad 0.2 < y < 0.97 \tag{46a}$$

This equation is not satisfactory in the ranges $y \to 1$ and $y \to 0$ and two other equations have to be introduced. In the high concentration range the data are correlated by:

$$(1-y) = 7.85\ (P_v/P)^{1.75}, \quad y > 0.97 \tag{46b}$$

Data for the low concentration range were not available. However, Henry's Law, previously used in the ammonia stripper calculations, may be applied in this concentration range. Henry's Law as given in Equation (27) may be rewritten in terms of mole fractions and psia.

$$P_{NH_3} = 1.07\ x/H_o \qquad \text{psia}$$

H_o is the Henry's Law coefficient as given by Equation (33). Substituting for x in Equation (44) yields:

$$y = (1 - P_v/P)/(1 - H_oP_v/1.07)$$

The denominator in this equation varies from 0.95 at 150°F to 0.90 at 500°F and may be considered constant over the temperature range corresponding to the dilute (lower) end of our fractionator. We also found that to match the available equilibrium data in the higher concentration range, and to ensure the correct limit $y \to 0$ as $(P_v/P) \to 0$, the denominator should be taken to be one. With some approximation we propose for the filute ammonia solutions:

$$(1 - y) = P_v/P \quad , \qquad y < 0.2 \tag{46c}$$

Note that Equation (46c) follows directly from Equation (44) as $x \to 0$.

(b) Liquid composition

The most satisfactory method for determining the liquid composition over the full concentration range was based on an Antoine type relationship:

$$\ln P = A - \frac{B}{t°F + 384} \qquad \text{(P in psia)} \tag{47a}$$

Both A and B are dependent on x.

Values of A and B were calculated for each tabulated x value using two extreme temperature data points. The calculated values, shown plotted in Figure 4-10, were found to be correlated by:

$$A = 14.49 - 1.90\ \{\sin (130x)\}^{1/2} \tag{47b}$$

$$B = 7036 - 3502\ \{\sin (100x)\}^{0.6} \tag{47c}$$

where the sine is to be taken of the numerical value in degress, not radians.

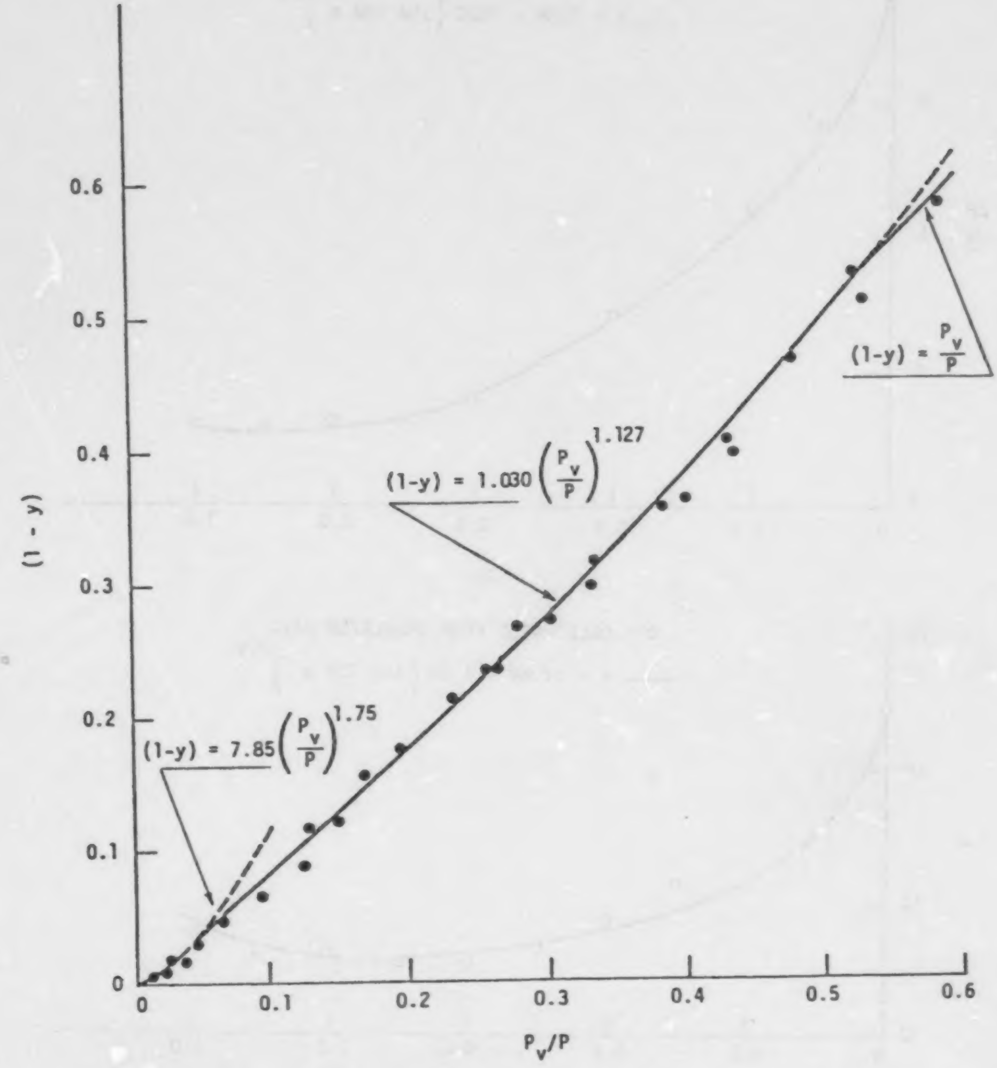


Figure 4-9. Ammonia concentration in vapor.

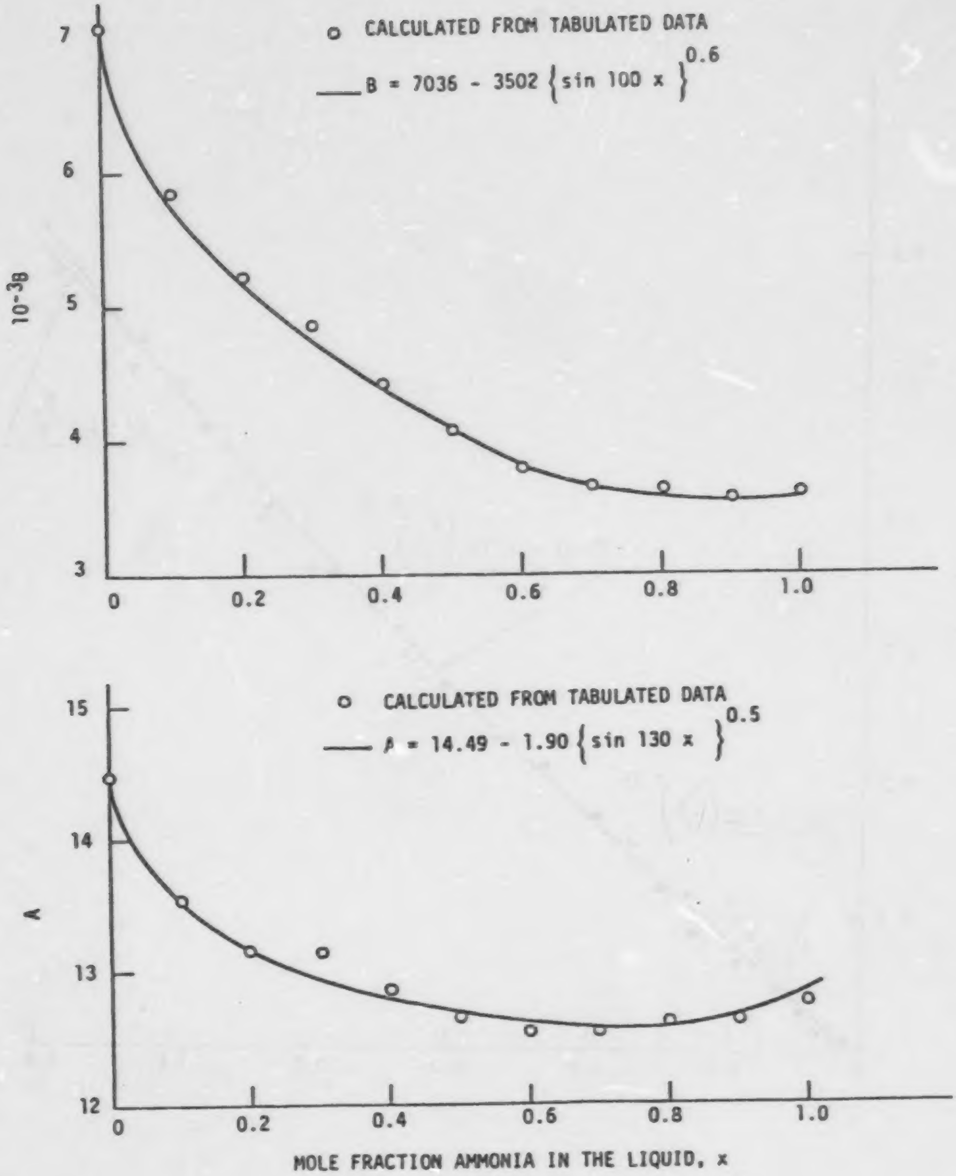


Figure 4-10. Determination of ammonia concentration in liquid.

Note that Equation (47) reduces to Equation (8), the vapor pressure expression for pure water, when $x = 0$. The liquid composition for a known pressure and temperature must be determined by trial.

Although highly empirical, Equation (47) yields liquid compositions within 5% of those presented in Reference 9. Differences of up to 10% exist between the data in Reference 8 and Reference 9. For very low liquid concentrations, $X < 0.02$, with known vapor composition, it is advisable to use the Henry's law expression, Equation (27).

4.4.2. Enthalpy Correlations for the Ammonia-water System

Enthalpy correlations are needed to determine the temperature gradient in the concentrated ammonia still. In Reference 9 liquid and vapor enthalpy data are tabulated against temperature and liquid composition, and against pressure and liquid composition. The liquid composition may be eliminated to obtain enthalpy as a function of temperature, with pressure the parameter as shown in Figures 4-11 and 4-12.

The liquid enthalpy is not strongly dependent on pressure over most of the concentration range, and a least squares fit to all the data (with a correlation coefficient of 0.97) gave:

$$H_\ell = 1.25t - 138 \ \text{Btu/lb}$$
$$100 < t°F < 400;\ 25 < P_{psia} < 250 \qquad (48)$$

The vapor enthalpy is strongly dependent on pressure, and is given by

$$H_v = 550 + \exp\{A + Bt\} \ \text{Btu/lb} \qquad (49a)$$

$$\text{in which } A = 1.5 + 0.00757P - 0.000027P^2 \qquad (49b)$$

$$\text{and } B = 0.0405\ P^{-0.233} \qquad (49c)$$

Equation (49) is accurate to within $\pm$ 10% in the range $90 \leq t°F \leq 400$, $25 \leq P\ \text{psia} \leq 250$.

4.4.3. Design Characteristics

The vapor-liquid equilibrium curves in Figure 4-8 show that lower pressure favor ammonia concentration. However, if we are making anhydrous liquid ammonia and wish to condense the overhead vapors using cooling water,

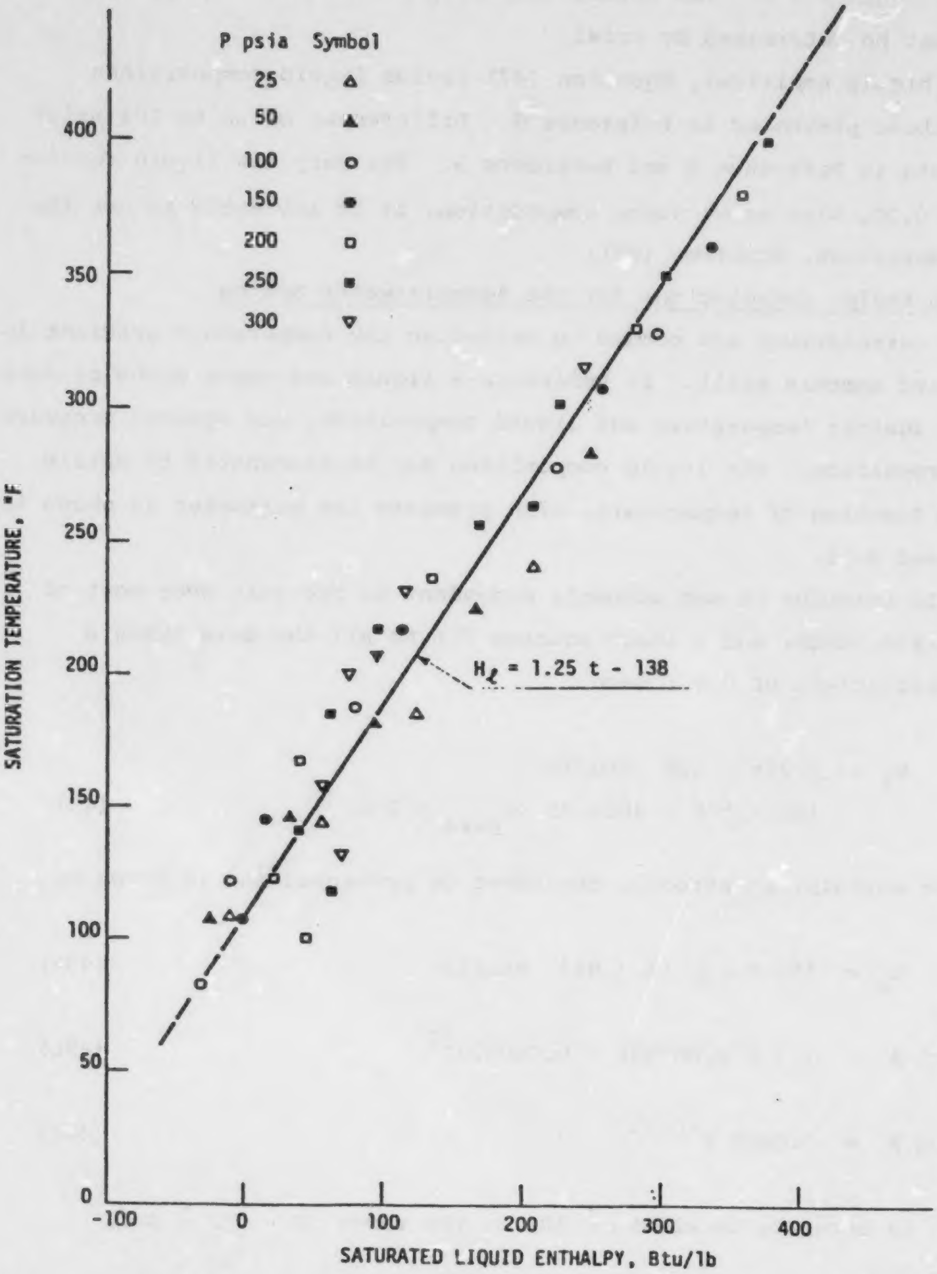


Figure 4-11. Liquid enthalpies of saturated ammonia-water.

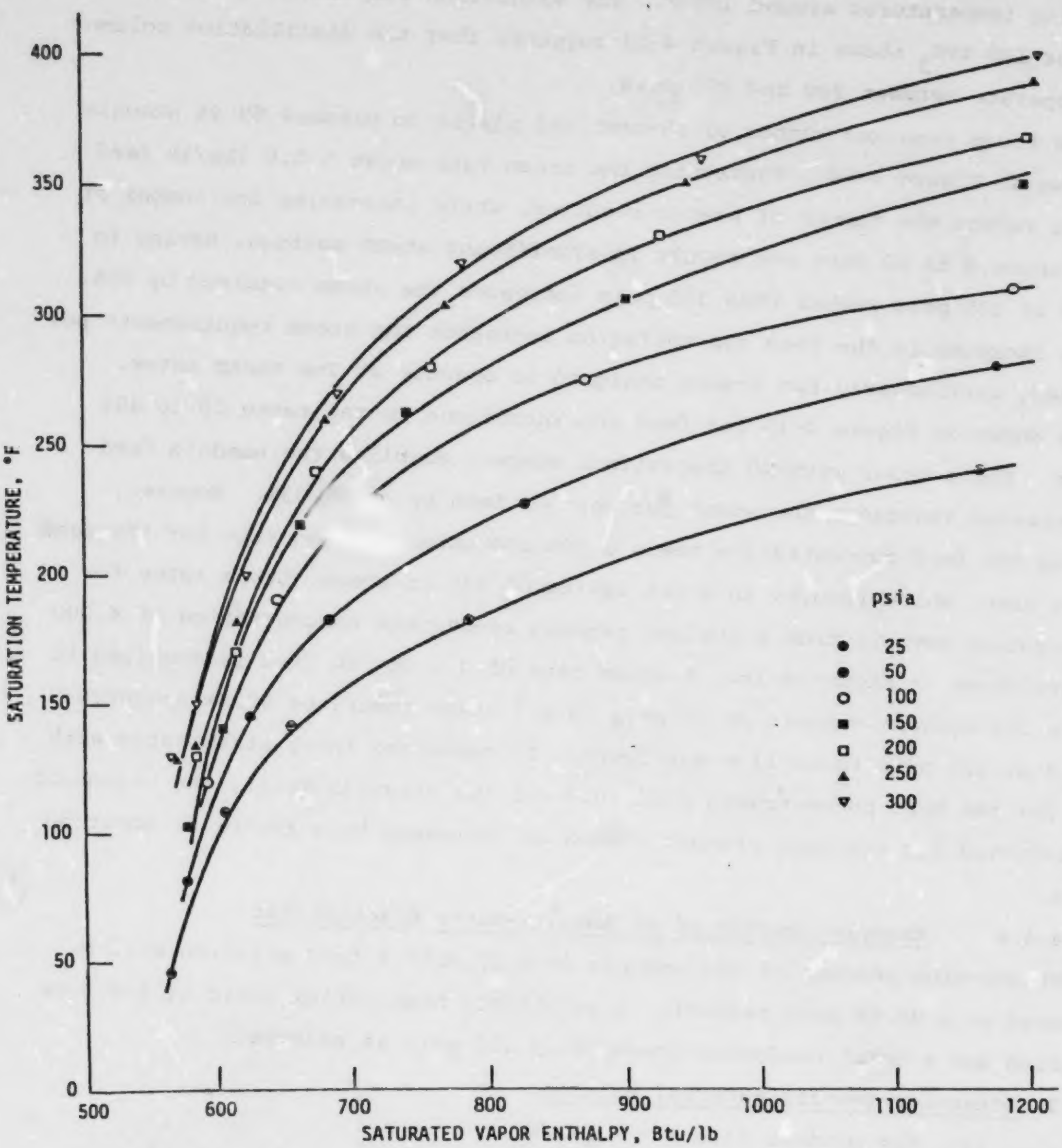


Figure 4-12. Vapor enthalpies of saturated ammonia-water.

then we have to operate at elevated pressures. Cooling waters are typically available at 80°-90°F and to keep condenser surface areas within practical limits, a cooling driving force of about 20°F is required which implies condensing temperatures around 105°F. The saturation temperature-pressure curve for 100 %NH_3 shown in Figure 4-13 suggests that the distillation column should operate between 200 and 250 psia.

The steam rate and number of theoretical plates to produce 99.9% ammonia are shown in Figure 4-14. Increasing the steam rate above ∿ 0.6 lbs/lb feed does not reduce the number of plates required, while increasing the number of plates above 8 to 10 does not result in significant steam savings. Having to operate at 225 psia rather than 150 psia increases the steam required by 25%.

An increase in the feed concentration increases the steam requirements per unit feed, particularly for towers designed to operate at low steam rates. This is shown in Figure 4-15 for feed concentrations in the range 20 to 40% ammonia. For a tower with 10 theoretical stages, doubling the ammonia feed concentration increases the steam per unit of feed by about 33%. However, doubling the feed concentration means a 50% reduction in feed rate for the same product rate, which results in a net saving of 33% in steam. Steam rates for concentrating ammonia from a typical process condensate concentration of 4,000 mg/l are shown in Figure 4-16. A steam rate of 0.2 lbs/lb feed is required to produce 30% aqueous ammonia at 25 psia in a 7 stage tower, or 99.9% anhydrous ammonia at 225 psia in an 11 stage tower. In comparing these steam rates with those for the more concentrated feed (0.4-0.6 lbs steam/lb feed), the volume of feed required for the same product volume is increased by a factor of about 50 to 100.

4.4.4 Example: Design of an Ammonia-Water Fractionator

Ninety-nine percent of the ammonia in a 30 mole % feed solution will be recovered as a 99.9% pure product. A relatively high reflux ratio of R = 2 is specified and a total condenser pressure of 225 psia is selected.

1. Determine overall material balance.

(a) The product rate $D = \eta FX_f/x_D$

$= 99 \times 0.3/0.999$

$= 29.73$

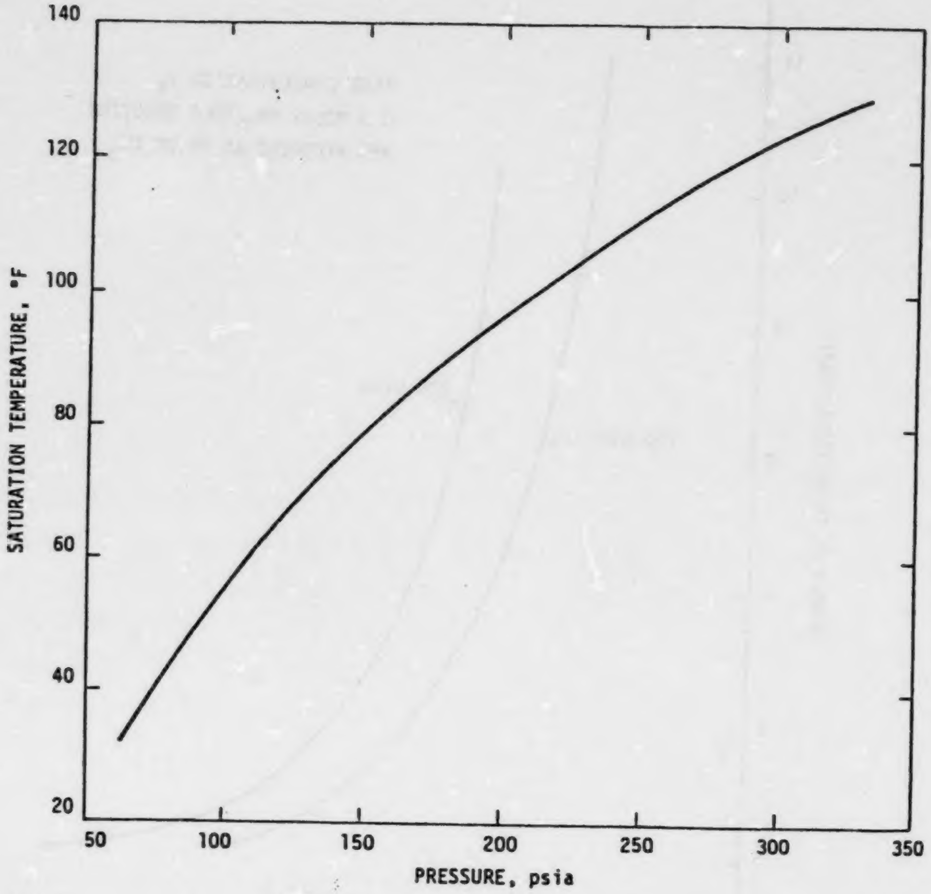


Figure 4-13. Pressure-temperature relation for saturated ammonia.

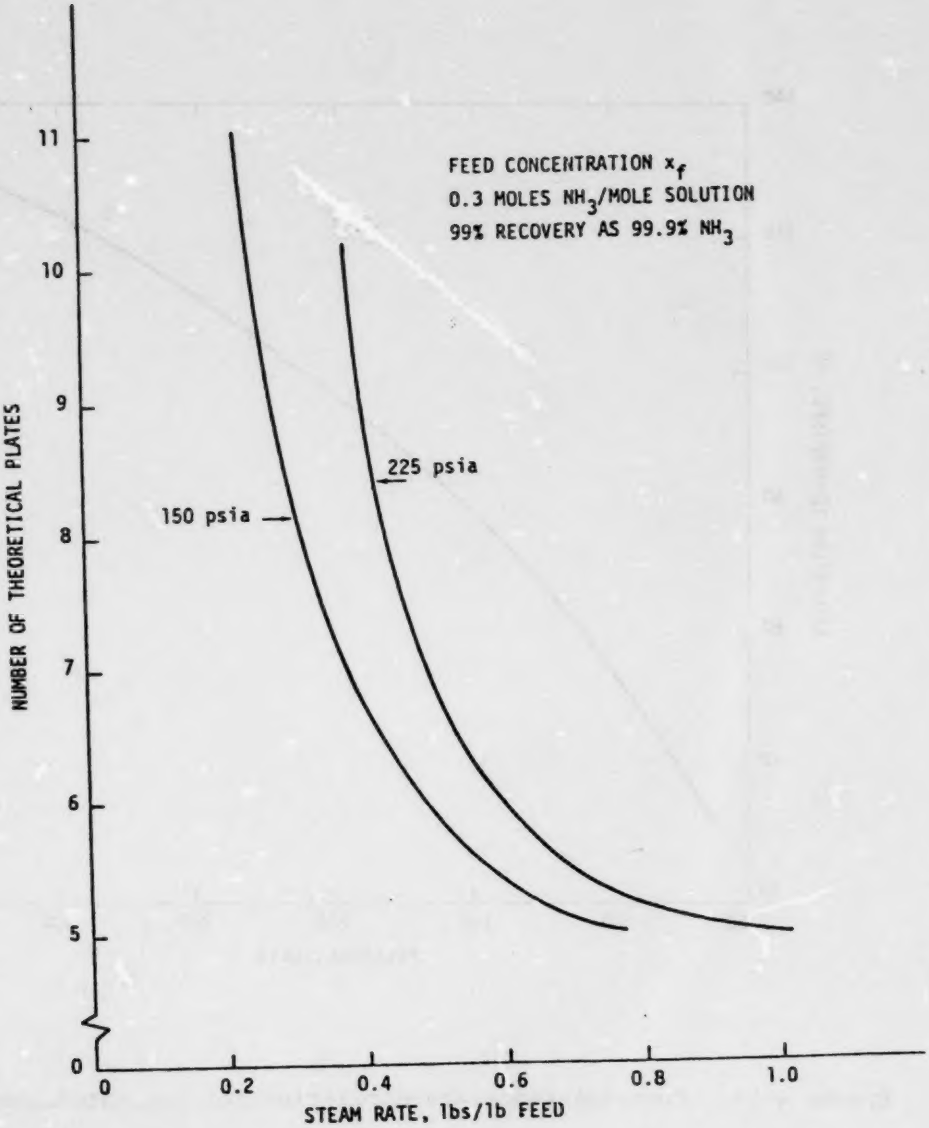


Figure 4-14. Steam required for ammonia distillation.

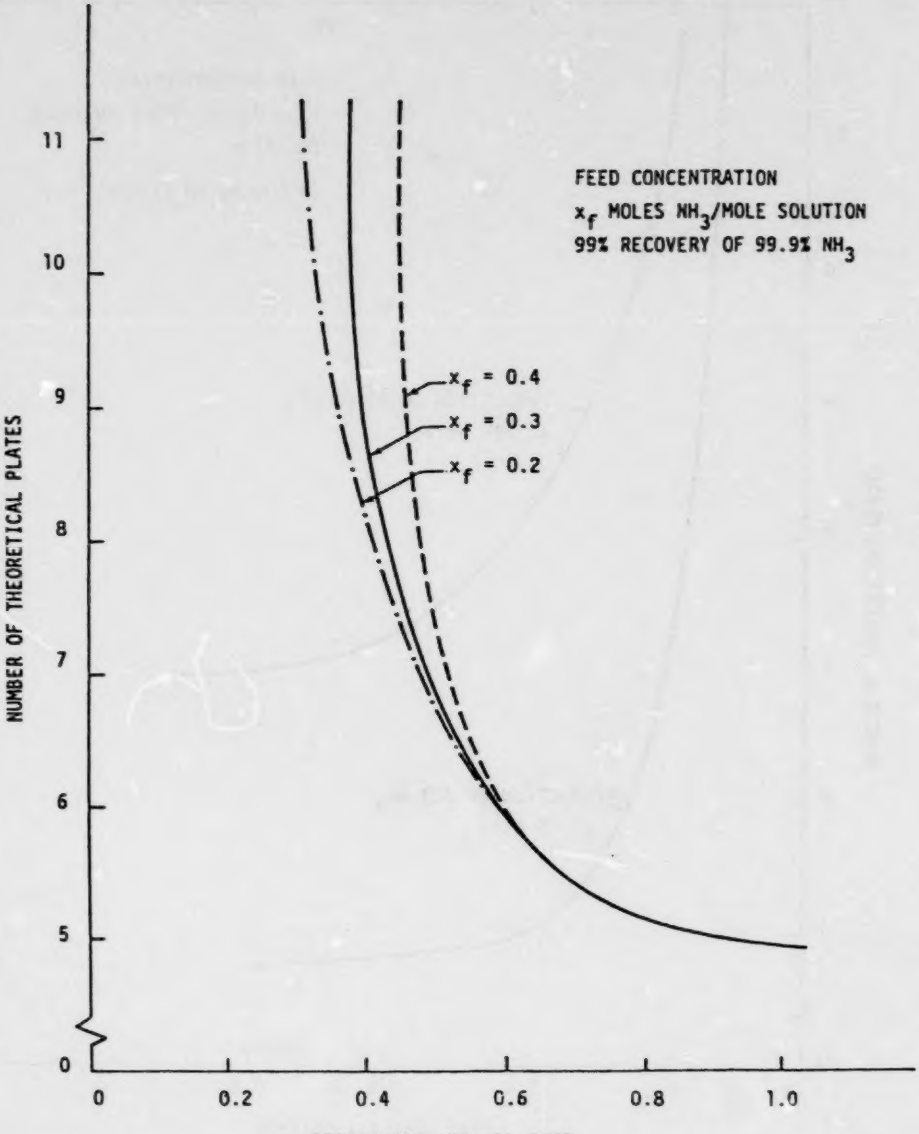


Figure 4-15. Effect of feed concentration on steam rate for ammonia distillation.

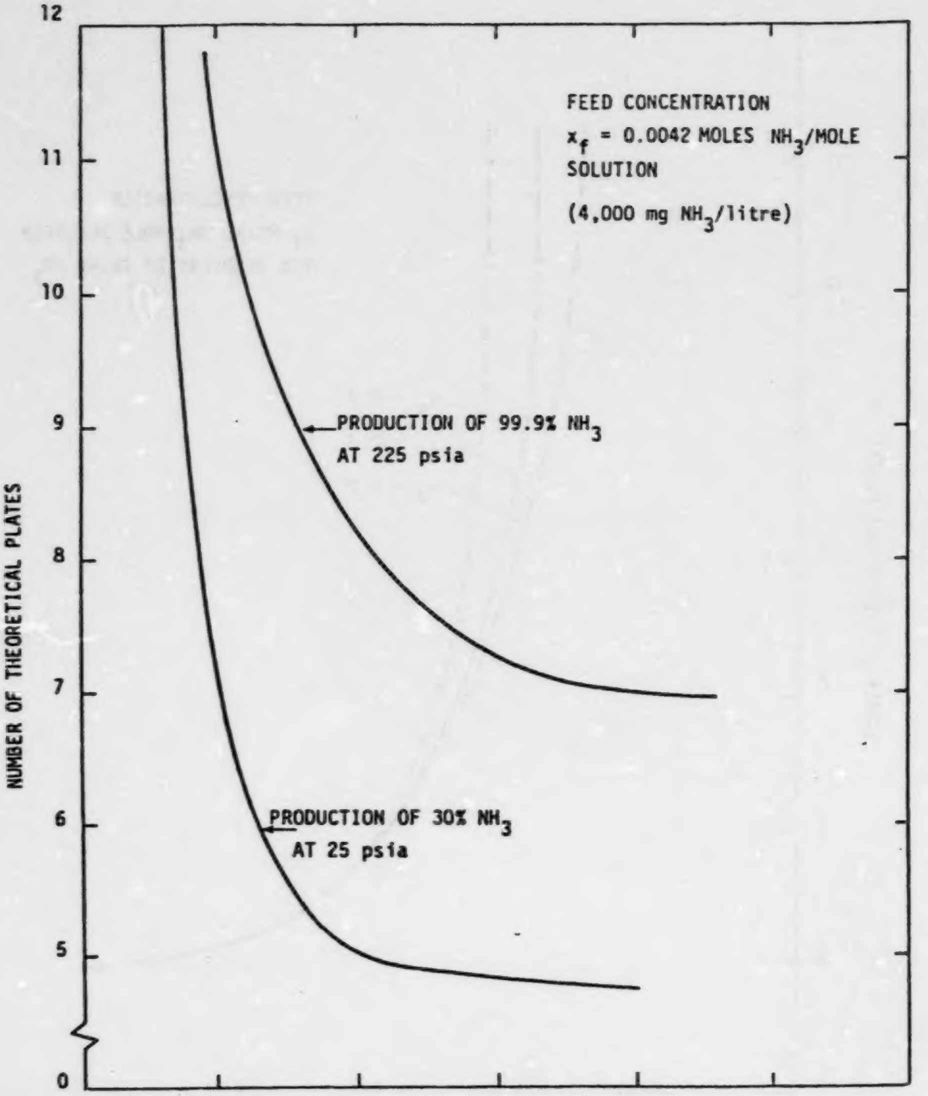


Figure 4-16. Direct distillation of process condensate.

(b) The vapor rate entering the condenser

$$V = D(R + 1)$$
$$= 29.73\ (2 + 1)$$
$$= 89.12$$

(c) The bottoms rate $B = F - D$

$$= 100 - 29.73$$
$$= 70.27$$

(d) The bottoms composition $X_B = (1 - h)\ FX_f/B$

$$= (1 - 0.99)(100)(0.3)/70.27$$
$$= 0.0043$$

2. Calculate temperature on the top plate.temperature.

The pressure of the first plate is taken to be 0.5 psi higher than the condenser pressure, so $P_1 = 225.5$ psia. From Equation (46b) for $y = 0.999$ we get $P_v/P_1 = 0.00595$ so that P_v, the water vapor pressure, is $225.5 \times 0.00595 = 1.341$ psia. The temperature corresponding to this water vapor pressure from Equation (8), is 111.6°F.

3. Calculate equilibrium liquid composition on the top plate.

A liquid mole fraction, $X = 0.9$, is first assumed. Substitution into Equations (47b) and (47c) gives:

$$A = 12.697 \text{ and } B = 3534$$

These values are in turn substituted into Equation (47a) to find the pressure on the plate, $P = 261$ psia. This is too high and a lower value for x must be tried. An ammonia mole fraction $x = 0.802$ gives $A = 12.619$, $B = 3575$, and a pressure of $P = 227$ psia. This is close enough to the actual pressure of 225.5.

4. Calculate the liquid rate from the top plate.

The liquid rate from a plate is determined by solving the enthalpy and material balances from the top of the column to the plate under consideration. The liquid and vapor enthalpies for the top plate ($t = 111.6$°F) are:

Liquid enthalpy, from Equation (48): $H_\ell = 1.50$ Btu/lb

Vapor enthalpy, from Equation (49): $H_v = 572.5$ Btu/lb

The enthalpy of the vapor leaving the next stage is determined by first assuming a temperature for that tray. The temperature will be about midway between the temperature of the preceding tray and the boiling point of water at the column pressure. We select $t_2 = 257.4$°F and get:

Vapor enthalpy, plate 2 from Equation (49): $H_v = 669.1$ Btu/lb

Substitution into Equation (39) yields the liquid rate from the top plate $L_1 = 46.6$.

The water vapor pressure and ammonia vapor concentration are calculated:

Water vapor pressure at 257.4°F, from Equation (8) = 33.8 psia
Mole fraction ammonia in vapor, Equation (46a) = 0.879

and substituted in Equation (37) to get a second estimate of the liquid rate $L_1 = 46.3$. The correspondence between the two calculated liquid rates indicates that the assumed temperature for stage 2, $t_2 = 257.4$°F, is correct. In cases where liquid rate determined by material balance is low relative to that determined by the enthalpy balance, a higher temperature must be assumed. Calculation of the liquid rate completes the information required for the first plate and we now proceed to the next plate.

6. Calculations for plate (n+1).

The temperature and vapor composition for each lower plate are found when determining the liquid rate for the previous plate. The vapor rate for plate (n+1) follows from Equation (35):

$$V_{n+1} = L_n + D - F$$

or, for plate 2:

$$\begin{aligned} V_2 &= 46.4 + 29.73 - 0 \quad (F = 0 \text{ above feed}) \\ &= 76.1 \end{aligned}$$

Steps 3 to 6 are repeated for successive stages until the liquid compositions are equal to or less than the calculated bottoms compositions $x_B = 0.0043$.

The results are:

Stage	x	y	V	L	T°F	Ppsia
1	0.802	0.999	89.1	46.4	111.6	225.5
2	0.260	0.879	76.1	161.0	257.4	226.0
3	0.066	0.458	90.7	164.3	346.3	226.5
4	0.011	0.113	94.0	167.4	382.1	227.0
5	0.0015	0.016	97.1	(70.3)	391.0	227.5

The liquid composition on stage 2 is just less than that in the feed, so the feed is introduced on stage 2. By stage 5, the liquid composition has fallen below the calculated x_B value, so stage 5 is the reboiler and the liquid rate is the bottoms rate calculated in Step 1.

7. Calculate the steam rate.

The steam required for fractionating is equivalent to the vapor leaving the reboiler. Since the molecular weight of the feed is 0.3 x 17 + 0.7 x 18 = 17.7, the steam rate on a mass basis is

$$\text{Steam rate} = (97.1 \times 18)/(100 \times 17.7) = 0.99 \text{ lb steam/lb feed}$$

4.5 Ammonia Recovery Using the Phosam-W Process

The Phosam-W process is a proprietary process of USS Engineers and Consultants Incorporated (UEC), a wholly-owned subidiary of U. S. Steel Corporation. The design procedure is quite complex and certain proprietary information is necessary; designs are made to order by UEC. We have given a brief description of the process and some of the interrelating effects involved in making a good design. The description shows why a complex computer program is used for designs and why rules of thumb are inadequate.

An exemplary process flow diagram is shown in Figure 4-17. There are four major pieces of equipment: (1) a water stripper in which volatile contaminants, ammonia and acid gases (carbon dioxide and hydrogen sulfide) are driven out of the wastewater; the wastewater passes on for subsequent treatment or use; (2) an absorber in which ammonia is absorbed out of the vapor into a solution; the acid gases pass on for further treatment or disposal; (3) a Phosam stripper in which the absorbing solution is regenerated for reuse and aqua ammonia is recovered; and (4) an ammonia still in which aqua ammonia is concentrated to anhydrous ammonia for sale or use.

(1) The Water Stripper

The water stripper is not proprietary and design procedures were given in Section 4.3.

It is usually economical to keep the stripper between 20 and 40 actual trays. In these systems with a low vapor rate compared to the liquid rate, tray efficiencies of between 25 and 50% are common. The higher efficiency is only realized with well-designed trays operated at 75 to 80% of flooding. If throughput is decreased, efficiency will fall. Twenty to forty actual trays

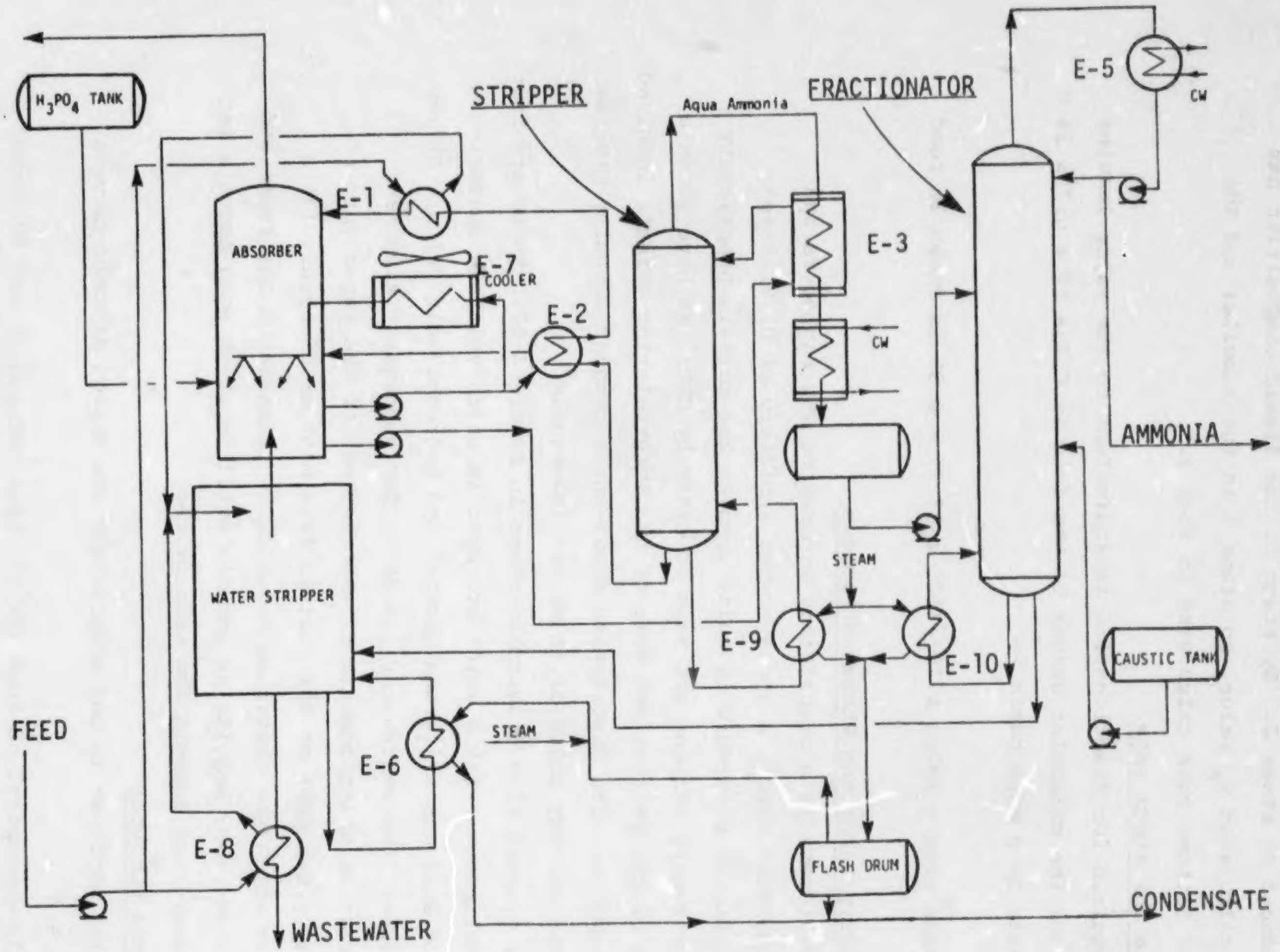

H$_3$PO$_4$ TANK
STRIPPER
Aqua Ammonia
FRACTIONATOR
E-5
CW
E-1
ABSORBER
E-7
COOLER
E-2
E-3
CW
AMMONIA
WATER STRIPPER
STEAM
E-9
E-10
CAUSTIC TANK
FEED
E-6
STEAM
E-8
FLASH DRUM
CONDENSATE
WASTEWATER

Figure 4-17. Phosam-W process for ammonia separation.

is in the range of 7-15 theoretical stages. Referring to Figure 4-4 we see that for 99% ammonia removal about 10 lbs steam per 100 lbs feed are required. In practice, steam rates of about 11-13 lbs per 100 lbs feed are reportedly[10] close to an economical optimum. Increasing the steam rate above this value without reflux increases the water vapor rate to the downstream absorber and may increase the cost of ammonia recovery. Ninety-nine percent ammonia removal is not always necessary for coal conversion plants since certain amounts of ammonia are tolerable or required in downstream processes.

Integration of the water stripper into the rest of the system serves to conserve energy. Wastewater is preheated partly by exchange with stripped water (Exchanger 8 in Figure 4-17) and partly by exchange with lean Phosam solution (Exchanger 1). If the ammonia concentration in the feed water is low, there will be a lot of water to preheat with not much Phosam solution to supply the heat. The rate of circulation of Phosam solution depends on the rate of feed of ammonia, not water. In this case steam preheat may be needed.

The water stripper may have a boiler or use live steam; it makes no difference to the overhead vapor. If live steam is used, the condensate enters the stream of stripped wastewater and is not recovered. If a reboiler is used, the steam must be at a higher pressure to provide enough temperature difference across the reboiler. A typical reboiler temperature is 290°F and a typical steam pressure for the reboiler is 64 psia.

Some of the water stripper steam duty may be provided by the reboil condensate of the two downstream towers, as well as bottoms from the ammonia fractionator. These streams are saturated at 200-300 psig, and ∿ 16% will flash at the water stripper conditions. The bottoms stream should be kept separate from the reboil steam and may be flashed directly into the water stripper as shown in Figure 4-17. The steam savings realized by utilizing reject heat from the fractionator is shown in Table 4-3. The steam saved by using condensate from the Phosam stripper reboiler is not included in Table 4 -3. A small quantity of caustic, added to the ammonia fractionator to control carbonate buildup, is introduced into the water stripper with the fractionator bottoms, and serves to free an equivalent amount of fixed ammonia.

TABLE 4-3. CALCULATED STEAM REQUIREMENTS FOR WATER STRIPPING AND AMMONIA FRACTIONATION. (BASED ON 100 LBS FEED AND 11 LBS STEAM TO THE WATER STRIPPER).

Ammonia Concentration		Fractionator			
Stripper Feed %	Fractionator Feed %	Feed lb	Steam (10 Stages) lb	Bottoms lb	Flash*(From Fractionator Bottoms and Reboiler) % Stripper Steam
0.6	10	6	1.74	5.4	10.0
	20	3	0.99	2.7	5.1
1.2	10	12	2.90	9.7	17.6
	20	6	1.98	4.9	9.6

---

*UEC states that flash from fractionator bottoms provides from 7 to 11% of water stripper steam requirements, depending on water stripper feed NH_3 concentration.

(2) The Absorber

The Phosam solution is phosphoric acid. A lean solution contains close to but more than one NH_4^+ per $PO_4^{\equiv}$ and a rich solution contains close to but less than two NH_4^+ per $PO_4^{\equiv}$. The solution is used inside the range of monoammonium phosphate with a little diammonium, and mostly but not 100% diammonium phosphate. The concentration of the solution is such that crystals do not form (probably below 120 g PO_4/l). Absorption requires a low temperature because the vapor pressure of ammonia over the solution decreases with the temperature. Absorption temperatures are usually kept below 220°F. This can be achieved by operating unrefluxed water strippers at a maximum of about 25 psia. The pressure drop for the vapor passing through the absorber is low and the acid gases leave at above atmospheric pressure.

Absorption is exothermic. The heat evolved per absorption of unit q quantity of solution (the differential heat of absorption) decreases as the ratio of $NH_4 : PO_4$ in solution increases. Since the absorption equilibrium is temperature dependent, the calculations are necessarily complex.

Cooling the absorber is necessary. Solution is pulled out of the absorber, cooled in Exchanger 7, and returned. (Exchanger 7 can be an air cooler.) Since the return is under pressure from the pump, it is sprayed into the absorber and the bottom section of the absorber is a spray. Above the spray section trays are used.

Cooling usually causes water to condense out of the vapor. This will always happen if the water stripper has no reflux so the water content of the vapor is high. Condensed water enters the circulating Phosam solution and passes to the Phosam stripper where it leaves in the aqua ammonia. Thus this cooling effects the concentration of the aqua ammonia to the ammonia still and hence the heat supply to the ammonia still. Optimization requires a balance here.

(3) The Phosam Stripper

To reverse the absorption reaction the pressure is raised, the temperature is raised, steam is passed through the solution to strip it, and heat is supplied because the desorption is endothermic.

Excessive steam for stripping is required if the pressure is below about 200 psig and 200-250 psig is usually used. If a reboiler is used, steam is usually required at 300 psig or above. Live steam can be used but this dilutes the aqua ammonia. If the water stripper has a reflux so that little water is condensed from the vapor, then it is often economical to use live steam in the Phosam stripper (except that the condensate goes to the wastewater stream). If the water stripper has no reflux, excessive dilution will occur if more than 50% of the steam to the Phosam stripper is live. Aqua ammonia is best recovered at not less than 10% NH_3 and cannot usually be recovered at greater than 20% NH_3. However, this range means a possible variation of two-fold in the feed to the ammonia still and has a considerable effect on the system economics. Thus, the use of live steam to the Phosam stripper requires careful evaluation.

Aqua ammonia is condensed in Exchanger 3 against rich solution and cooling water. Aqua ammonia is not refluxed to the Phosam stripper. The Phosam stripper feed temperature can be controlled to condense more or less vapor from the top tray. This affects the aqua ammonia feed strength and the plant water balance.

(4) The Ammonia Still

Design procedures were discussed in Section 4.4 where it was shown that steam rates are slightly dependent on the concentration of the aqua ammonia, but will generally be in the range 0.2-0.4 lb steam per lb feed. If a reboiler is not used, the steam condensed passes to the wastewater after recovering residual heat by flashing in the water stripper.

The ammonia still will plug up if tramp oils are not released and if caustic soda is not added to dissolve carried over carbon dioxide. These important procedures are proprietary to UEC.

4.6 Ammonia Recovery as Ammonium Sulfate

Ammonia is removed from the ammoniacal liquor in a water stripper and bubbled through dilute (approximately 60%) sulfuric acid to form ammonium sulfate crystals. The crystals, which may contain some tars and free acid, are suitable for use as fertilizer. Process flow sheets for ammonium sulfate production are described in the literature[14].

Modern plants must be designed so that the acid gases, which are not dissolved in the sulfuric acid, do not become a pollution problem. If dilute sulfuric acid is not a process by-product, then from considerations of both transport and materials of construction it might be more economical to use concentrated acid.

The economy of the ammonium sulfate process depends on the market prices of ammonia and ammonium sulfate. Depending on the quality of the ammonium sulfate, its market value (FOB) will be from about 30% to 50% of that of ammonia. However, the ammonium sulfate market is variable, shipping costs are high, and the quality of the product will probably be such that the anticipated market value is at the lower end of this range. This is little more than the ammonia content of the salt, so the costs of sulfuric acid will not be recovered. Recovery of ammonia wastes as anhydrous ammonia is feasible, and the projected ammonia market appears to be stable[15]; therefore, the ammonium sulfate route is not recommended.

4.7 Ammonia Recovery by the All-Distillation Process

This process consists of two distillation columns. In the first, the acid gases are stripped with steam while the ammonia is held in solution. In the second column, the ammonia is concentrated; either a 30% aqueous ammonia, or anhydrous ammonia may be produced.

Details of the all-distillation system, known as the CLL (Chemie-Linde-Lurgi) process are proprietary. Lurgi has proposed this system for their El Paso and Wesco plants[16], and claims that it is economically more attractive than other processes for ammonia recovery in large plants. It is not known how the ammonia is held in solution in the CLL process. One method would be to provide a wash stream to the top of the stripper (see Figure 4-16). The wash water would exit with the tower bottoms and form part of the feed to the ammonia concentrator, so increasing the steam requirements of this unit. Another method would be to fix the ammonia with acid. The fixed ammonia must then be released by addition of alkali; milk of lime is usually used. The addition of chemicals means increased costs and an increased TDS of the wastewater, and may lead to carbonate plugging of the ammonia concentrator. It is possible that a combination of wash and chemical additives are used in the proprietary process. If chemical additives are not used, the separation will depend on the relative volatilities of the gases.

The volatility of H_2S relative to NH_3 in a system containing only H_2S, NH_3 and H_2O is shown in Figure 4-18. To increase the relative volatility, and thereby facilitate the separation of H_2S from NH_3, the temperature and/or the H_2S concentration must be increased. Of course the H_2S concentration drops as stripping proceeds, and high temperature (pressure) operation is therefore selected. Chevron[13] indicates operation at 100 psig, but also indicates recycle of what appears to be concentrated ammonia to the H_2S stripper. (See Figure 4-19.) This is not understood since we know from Figure 4-18 that increasing the ammonia concentration decreases the volatility of H_2S relative to NH_3.

The relative volatility of CO_2 and NH_3 in systems containing CO_2, NH_3 and H_2O is shown in Figure 4-20. The relative volatility of CO_2 is an order of magnitude greater than that of H_2S at low temperatures, and increases rapidly with temperature. CO_2 is therefore considerably easier to separate from NH_3.

The effective relative volatilities may be increased by using wash and/or reflux. Wash will hold down the less volatile component in the overhead as will reflux. We found that a total condenser should be used to provide the reflux since this increases the concentration of the more volatile component and also increases its relative volatility (Figures 4-18 and 4-20).

We investigated stripping 99% of the CO_2 while holding down 95% of the ammonia in an H_2S free Lurgi type process condensate (Table 4-1), using wash rates of 25% to 100% of the feed rate and the reflux necessary to achieve the specified separation. Some results are shown in Figure 4-21. Several combinations of steam rate and reflux yield the desired separation for each wash rate selected; however, we did not search all possibilities and these results may not be optimum.

The cost of the wash and reflux can be approximated as follows: the ammonia fractionator requires high pressure steam at about 0.2 lb/lb feed; at a steam cost of \$2.5 per 10^3 lb, additional steam due to the use of wash costs \$0.5 per 10^3 lb wash used. About 10^6 Btu must be removed in the condenser for each 10^3 lb reflux; if cooling water costs 12¢ per 10^3 gals circulated, reflux costs \$0.6 per 10^3 lb reflux. In addition, the capital cost of the condenser, amortized at 19%/yr, amounts to \$0.03 per 10^3 lb reflux. These costs are shown in Figure 4-22 and suggest that the optimum operation will be with small wash rates and at high pressure. The small differences in steam rate in the acid gas stripper, and the dependence of the cost of this stripper on pressure are not included in Figure 4-22, but they do not significantly affect these findings.

In Figure 4-22 we see that in addition to the usual costs for stripping and ammonia fractionation, an additional \$1 to \$2 per 10^3 gallons is required to separate the acid gas and ammonia by this method. By comparison, the value of ammonia in a condensate containing 17,000 mg is nearly \$8 per 10^3 gals.

We emphasize that our findings here are based on our theoretical stripper design procedure (Section 4.3); they may not be achievable in practice and they do not reflect any proven commercial process.

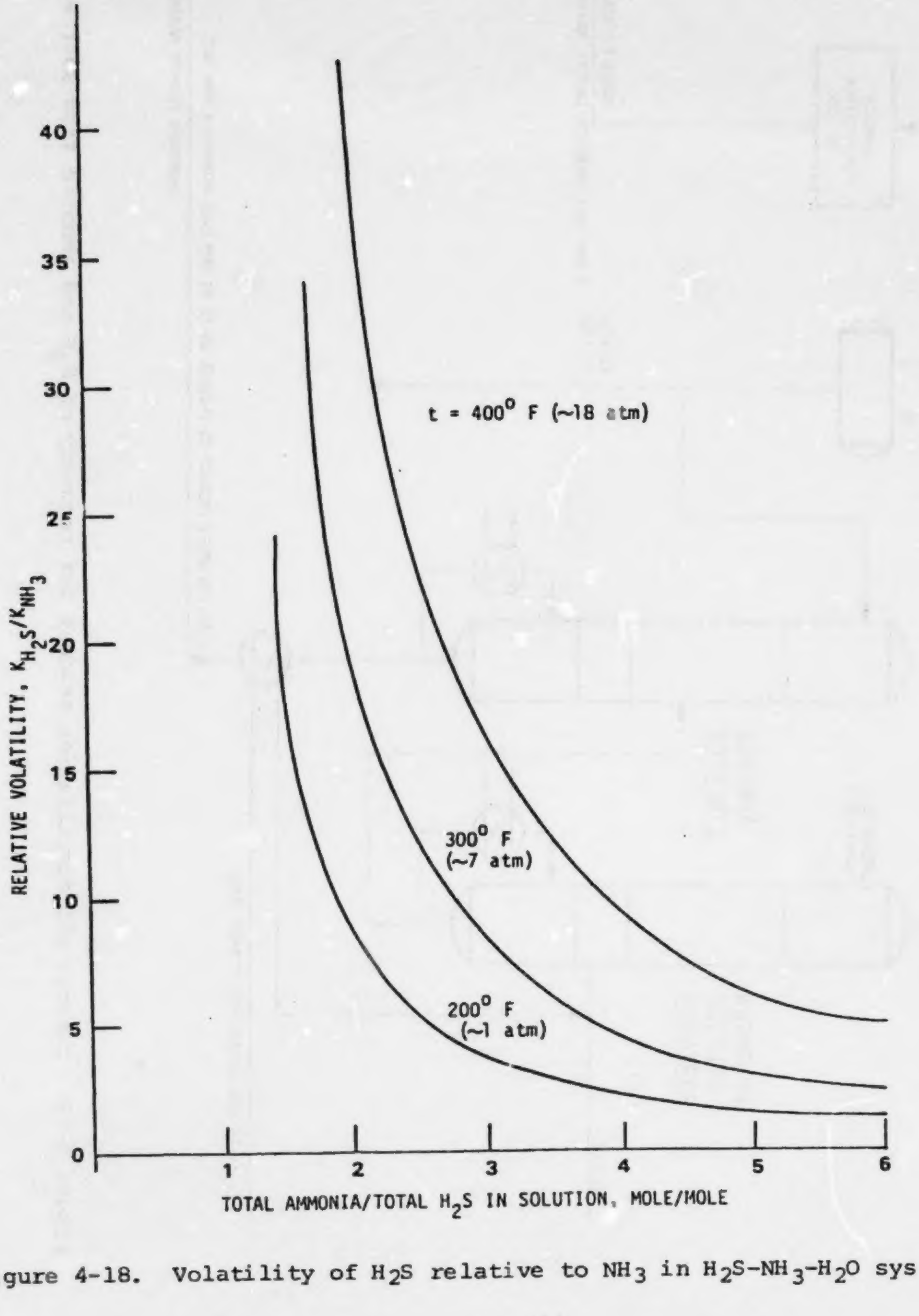


Figure 4-18. Volatility of H_2S relative to NH_3 in H_2S-NH_3-H_2O systems.

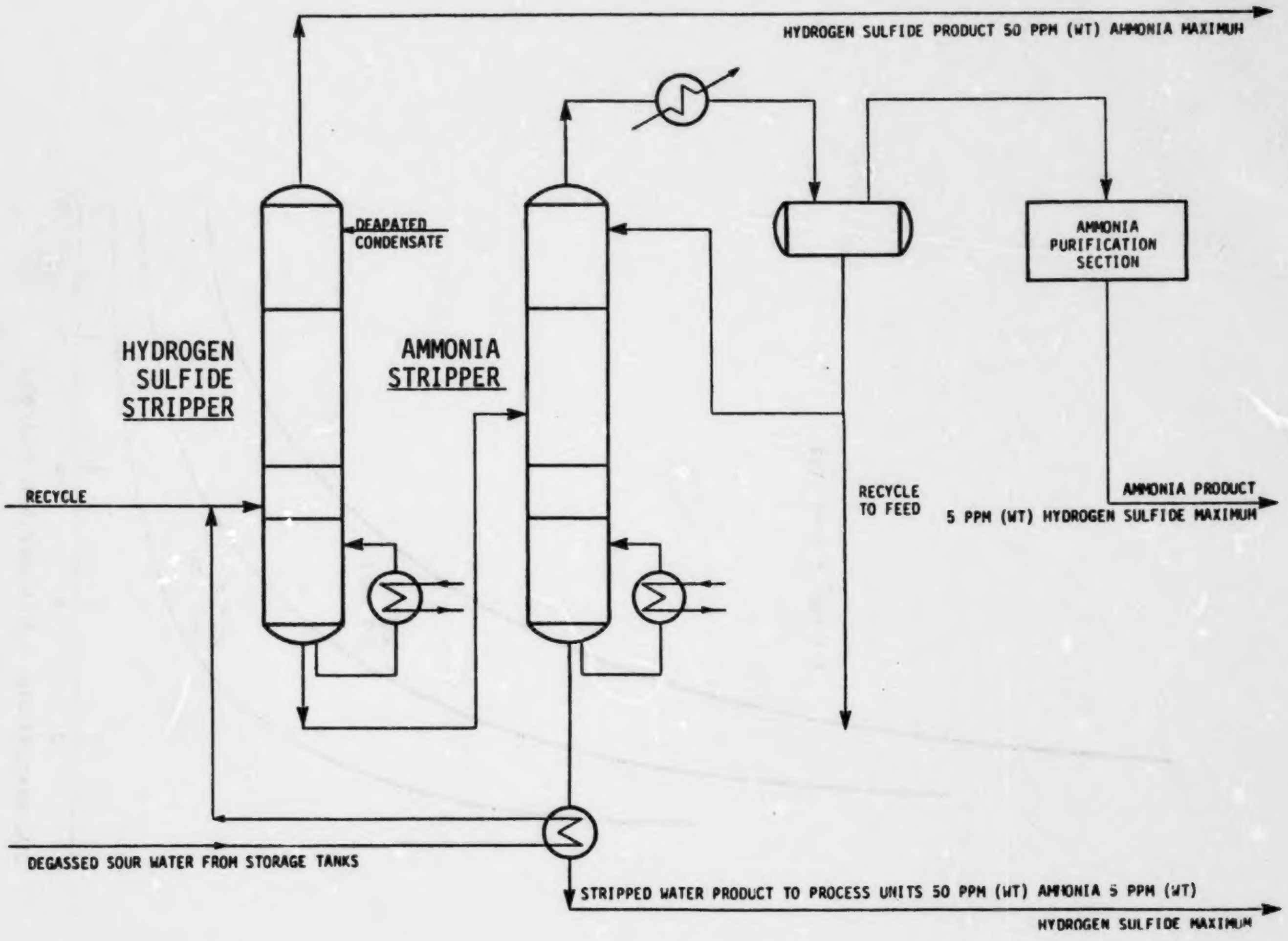

HYDROGEN SULFIDE PRODUCT 50 PPM (WT) AMMONIA MAXIMUM
DEAPATED CONDENSATE
HYDROGEN SULFIDE STRIPPER
AMMONIA STRIPPER
AMMONIA PURIFICATION SECTION
RECYCLE
RECYCLE TO FEED
AMMONIA PRODUCT
5 PPM (WT) HYDROGEN SULFIDE MAXIMUM
DEGASSED SOUR WATER FROM STORAGE TANKS
STRIPPED WATER PRODUCT TO PROCESS UNITS 50 PPM (WT) AMMONIA 5 PPM (WT)
HYDROGEN SULFIDE MAXIMUM

Figure 4-19. Chevron all distillation process for recovery of H_2S and ammonia from sour waters.

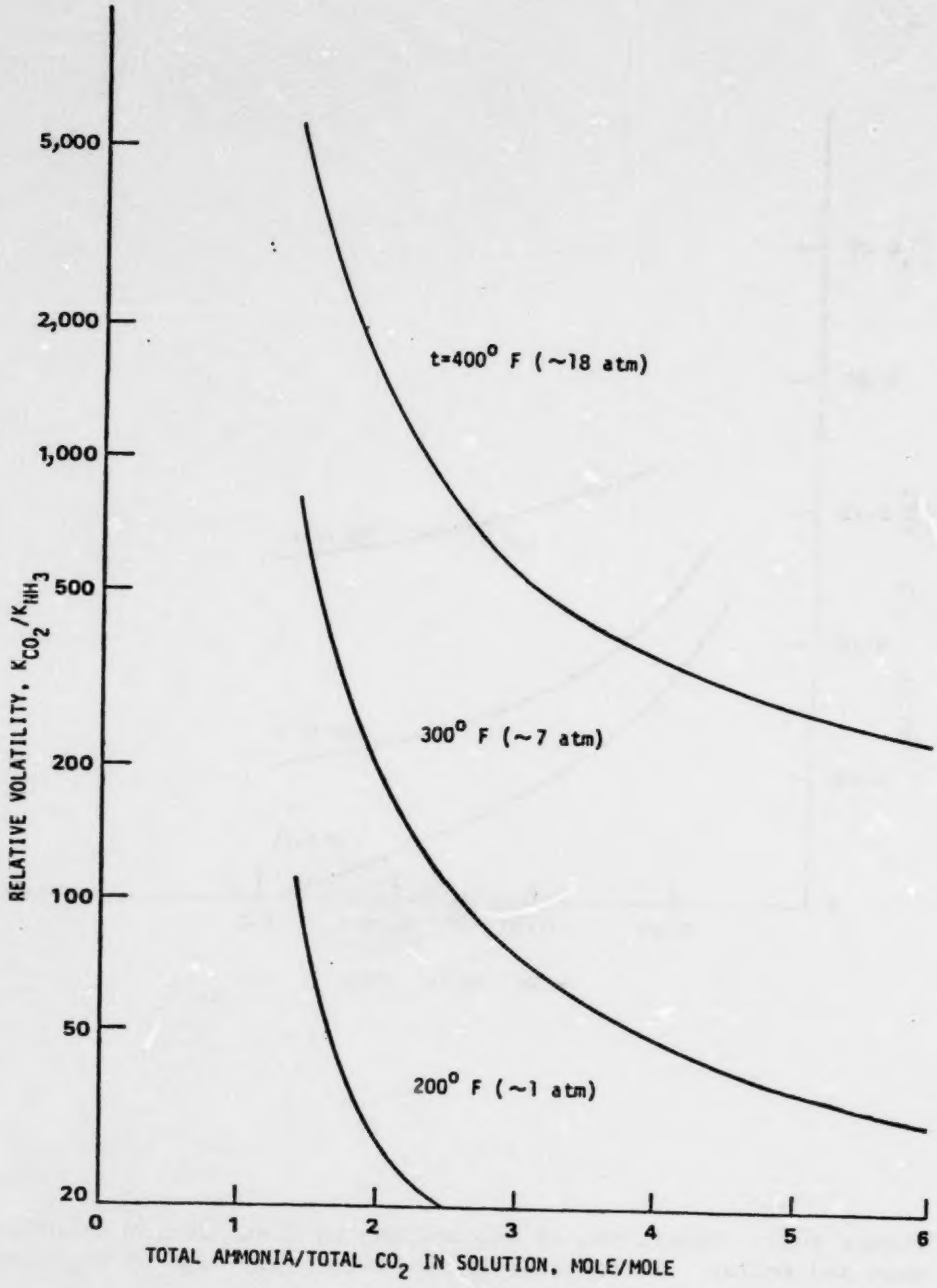


Figure 4-20. Volatility of CO_2 relative to NH_3 in CO_2-NH_3-H_2O systems.

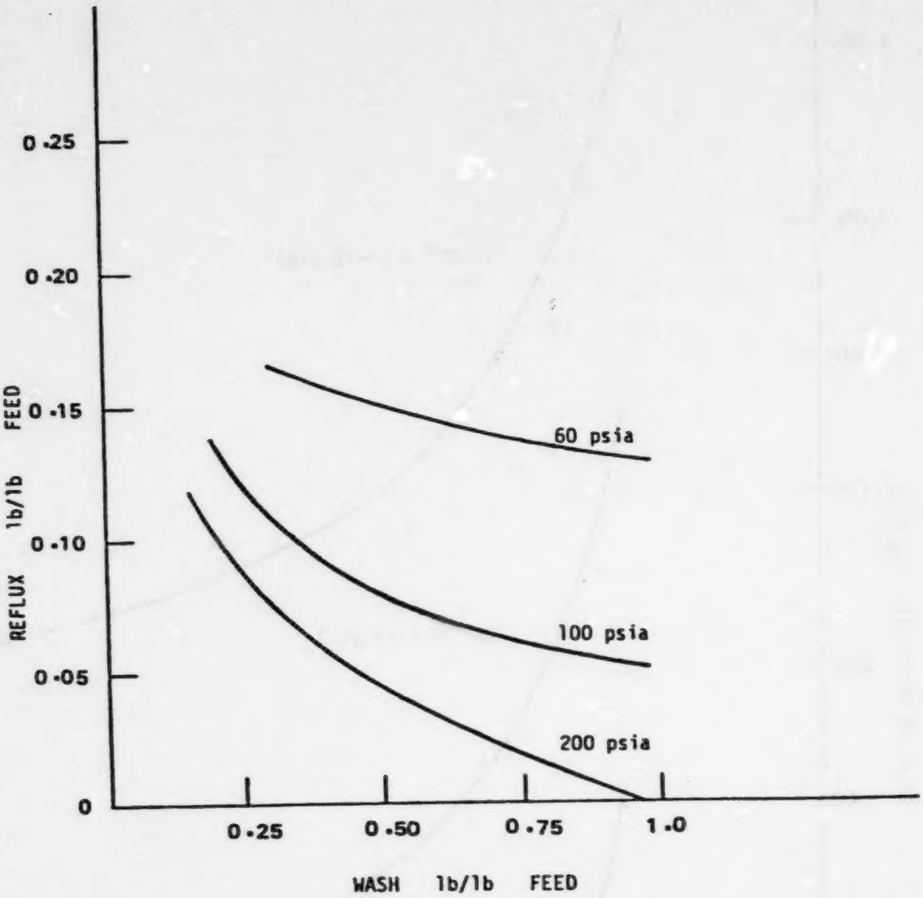


Figure 4-21. Separation of CO_2 and NH_3 by distillation using water wash and reflux. Stripper specifications: 99% CO_2, 5% NH_3 removal.

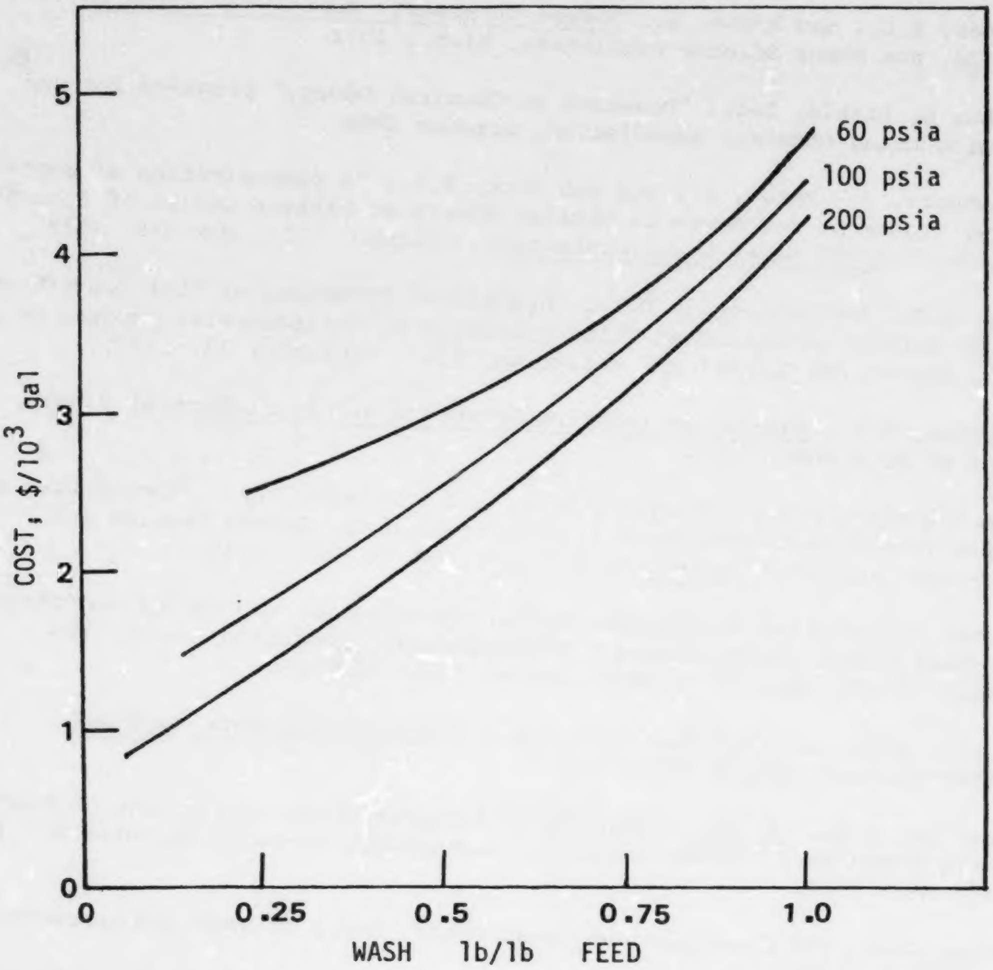


Figure 4-22. Cost of holding down ammonia when stripping CO_2. Condenser cooling water costs, condenser capital costs (19%/yr), and costs of additional steam for ammonia fraction only. Reflux rates required as per Figure 4-21.

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5. BIOLOGICAL TREATMENT

Biological oxidation is the process in which living organisms, mostly bacteria, cause the reaction of dissolved oxygen with dissolved and suspended organic molecules to make more organisms and small residual molecules, mostly carbon dioxide. The result is water cleaned of most of its organic content and a settleable, separable sludge of dead and living bacteria. Very approximately, less than half the weight of BOD (biochemical oxygen demand) is converted to weight of sludge.

In the absence of much carbonaceous matter bacteria will flourish which can oxidize ammonia to nitrate. This process is nitrification. The water is now passed to a separate vessel in which oxygen is withheld. Different bacteria will use the oxygen in nitrate leaving the nitrogen in the molecular form; this is denitrification. Selected carbonaceous materials, usually methanol, must be added to a denitrification reactor. Nitrification and denitrification are expensive and are probably not suitable for removing the massive quantities of ammonia found in wastewaters from fuel conversion plants.

In the absence of oxygen bacteria will convert organic matter to more bacteria and methane. This is anaerobic treatment and it has the particular advantage of not requiring a large energy input for oxygenation or aeration. However, evidence is lacking that anaerobic treatment will function smoothly on wastes from coal conversion.

Not all organic molecules are susceptible to biological oxidation; those that are not are biorefractory. One measure of the content of biorefractory molecules in water is the ratio of chemical oxygen demand to biochemical oxygen demand (COD/BOD). If the ratio is high, there are many molecules that are chemically oxidizable and not biologically oxidizable. When the ratio is greater than about two, the water is considered to have a large amount of biorefractory content. All available evidence is that wastewaters in coal conversion are predominantly biodegradable and that biological oxidation is a functional treatment. This does not mean that it is economical at all flow rates and concentrations.

Many biodegradable molecules are toxic to bacteria in high concentrations. In particular phenol, which is rapidly biodegradable at low concentrations, must usually be kept below 500 mg/l in the reaction tank. Ammonia in high concentration is also toxic, but it will be removed before biological treatment.

Biological oxidation requires the presence of bacteria, organic matter and dissolved oxygen. For most wastes the concentration of bacteria yielded by a once-through reactor is not high enough to obtain on adequate rate of reaction. It is usual, therefore, to separate the sludge from the slurry leaving the oxidation tank and return much of it to the tank; the balance of the sludge is disposed of. This procedure maintains a high bacterial concentration in the reactor at all times and is called the activated sludge process. Another way to obtain high concentration of bacteria is to grow the bacteria on a solid surface and to pass the wastewater in a thin film over the surface which is the principle of a trickle filter.

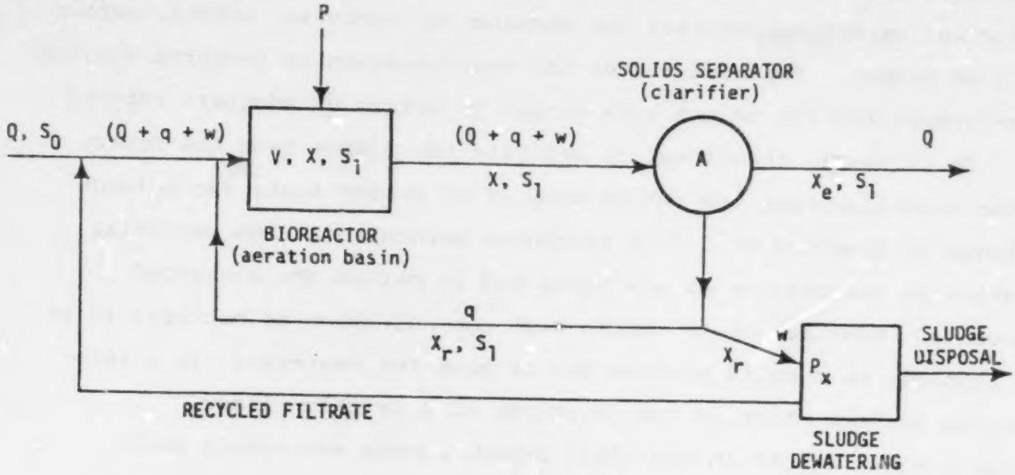
The biological agents in municipal sewage plants are simply soil bacteria. More efficient will be the sludge taken from a plant treating coke oven wastewater which is phenolic. These bacteria are acclimated to a phenolic waste and will grow more quickly than unacclimated bacteria. Acclimated sludge is available[23]. Bacteria deliberately mutated for acclimation to phenol are also available and seem to be even more efficient[26,27].

The oxidant can be air or oxygen. In municipal sewage plants air is the most common oxidant. It is necessary to stir the bioreactor to keep the sludge in suspension. If the stirrers are located so that they also pull air into a vortex in the tank, the oxidant addition is obtained for only a modest increase in energy consumption over that needed for stirring. While municipal sewage may have only 200 mg BOD/l, the wastes from coal conversion plants will have up to 20,000 mg BOD/l. Thus, the use of simple surface aerators will consume a lot of energy. Surface aerators may need 0.4 to 0.45 kw-hrs/lb BOD removed. For 15,000 mg BOD/l removed this translates to 50-56 kw-hr/thousand gallons, therefore, it may easily be more economical to use oxygen instead of air. Most coal conversion plants are making oxygen on site in any case.

For background information the reader is referred to References 28, 29, 34 and 45. The use of oxygen is described in References 30 and 31; a description of anaerobic treatment is given in Reference 32; a combination of trickle filters and activated sludge are described in Reference 33.

5.1 Air Activated Sludge (AAS) Process

The activated sludge process is widely used, mostly in municipal sewage treatment plants. On Figure 5-1. is shown a scheme appropriate for


P
Q, S0
(Q + q + w)
V, X, S1
BIOREACTOR
(aeration basin)
(Q + q + w)
X, S1
SOLIDS SEPARATOR
(clarifier)
A
Q
Xe, S1
q
Xr, S1
Xr
w
Px
SLUDGE DISPOSAL
SLUDGE DEWATERING
RECYCLED FILTRATE

Q = flow rate of liquid waste to be treated biologically, volume/time;

q = flow rate of recycled sludge, volume/time;

w = flow rate of wasted sludge, volume/time;

S_0 = influent substrate concentration, mass/volume;

S_1 = effluent substrate concentration, mass/volume;

X = microbial mass concentration, mass/volume;

X_e = microbial mass concentration in the clarified overflow from the solids separator, mass/volume;

X_r = microbial mass concentration in the underflow from the solids separator, mass/volume;

P = power requirement for aeration, energy/time;

P_x = excess microorganisms production rate, mass/time.

V = volume of aeration basin

Figure 5-1. Air activated sludge material.

foul process condensates. The feed will have to be from a storage pond or tank to keep changes in the flow and concentration to the bioreactors as slow as possible. Phosphorus, an essential nutrient for the bacteria, will have to be added. The bioreactor is one or more stirred basins arranged in series and the concentration of organic waste in the reactor is close to the concentration in the water leaving the reactor. By carefully distributing the concentrated feed, the toxicity of high concentrations of phenol can be avoided.

Design equations and two examples will be given for this process.

5.1.1 The Biokinetic Model. The biokinetic model developed by Lawrence and McCarty[2,28] has been widely used for the activated sludge process and will be used here. It is primarily based on a relationship between substrate utilization and microbial growth, which can be formulated in two basic equations. The first equation is an empirically developed relationship between the net growth rate of microbes and the rate of substrate utilization:

$$\frac{dX}{dt} = Y \frac{dS}{dt} - k_d X \qquad (1)$$

where X = concentration of microorganisms
t = time
Y = growth yield coefficient; weight of microorganisms produced per weight of substrate removed
S = concentration of substrate or degradable contaminant
k_d = microorganism decay coefficient, time^{-1}

If Equation (1) is divided by X, we obtain:

$$\frac{1}{X}\frac{dX}{dt} = \frac{Y}{X}\frac{dS}{dt} - k_d \qquad (2)$$

In Equation (2) each term has the dimension (time^{-1}) and compatible units must be used. The lefthand side of Equation (2), which is the rate of increase of concentration of microorganisms per unit concentration, may also be written $1/\theta_c$, where 0_c is called the mean cell residence time, or sludge age. The first term on the righthand side of Equation (2) includes the quantity $\frac{1}{X}\frac{dS}{dt}$, which is the rate of decrease of concentration of substrate per unit concentration of microorganisms, often described as F/M ratio.

The quantity $\frac{1}{X}\frac{dS}{dt}$ = F/M is a function of the concentration of substrate and the second equation of the Lawrence and McCarty model assumes the function:

$$\frac{1}{X}\frac{dS}{dt} = \frac{kS}{K_s + S} \tag{3}$$

The coefficients k and K_s in Equation (3) may be evaluated by plotting $\frac{1}{X}\frac{dS}{dt}$ versus S, and the values of Y and k_d in Equation (2) can be determined by plotting $\frac{1}{X}\frac{dX}{dt}$ versus $\frac{1}{X}\frac{dS}{dt}$. Typical plots prepared by us are shown in Figures 5-2 and 5-3 using data from the AAS at the Bethlehem Steel/Coke Plant[23]. Other possible values for k, K_s, Y and k_d will now be discussed.

5.1.2 Values of the Kinetic Constants. Reports are available on three wastewaters of interest. The first is coke oven liquor investigated at Bethlehem Steel[23]. Biokinetic constants were not derived in Reference 23, but we have plotted the data from Reference 23 in Figures 5-2 and 5-3. The data and the plots both use phenol as the substrate. To convert to BOD we used 2 lb BOD ≡ 1 lb phenol which is the usual experience (the theoretical oxygen demand is 2.38 lb/lb phenol). This gives the constants shown as Set No. 1 in Table 5-1. The constants shown as Set No. 2 were derived by us from experimental results on an H-Coal wastewater[25] and the constants shown as Set No. 3 are for the Synthane process using a Montana Rosebud coal[37,38]. The sets of constants are quite different.

TABLE 5-1 BIOKINETIC CONSTANTS

	No. 1 Coke Oven Liquor	No. 2 H-Coal Wastewater	No. 3 Synthane Wastewater
k, g soluble BOD/g MLVSS day	1.8	∿ 0.3	∿ 1*
K_s, mg BOD/l	0.34	∿ 30	∿ 266*
Y, g VSS/g BOD processed	0.2	0.48	0.37
k_d, day^{-1}	0.17	0.03	0.033
Temperature °C	27-32	23	

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*Estimated on the basis of 1 g TOC ≃ 2 g BOD

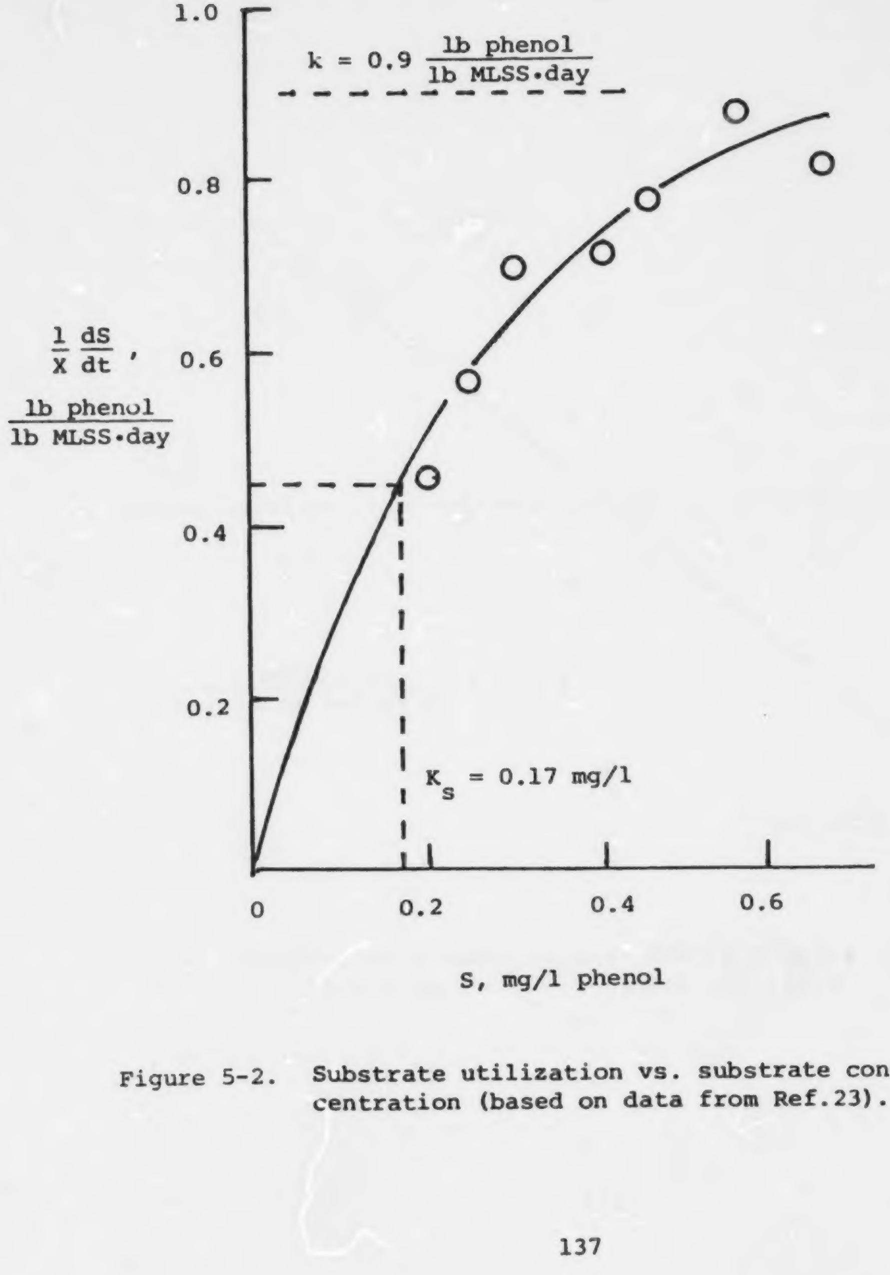


Figure 5-2. Substrate utilization vs. substrate concentration (based on data from Ref.23).

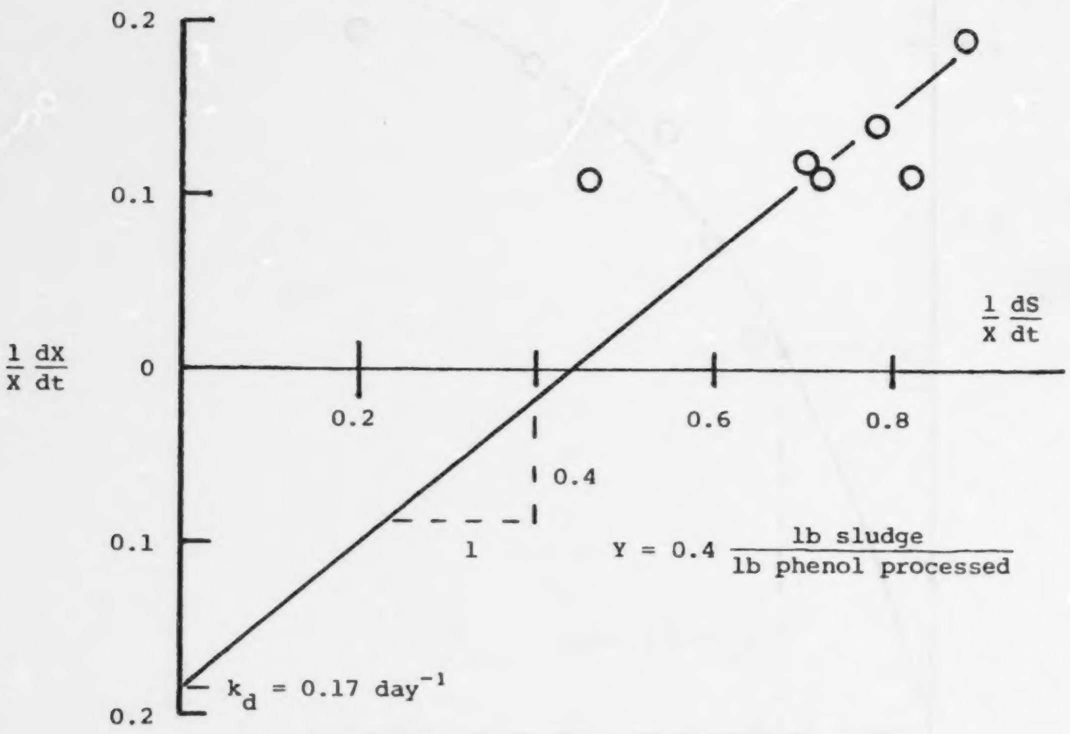


Figure 5-3. Sludge growth rate vs. substrate utilization rate (based on data from Ref.23).

In Table 5-2 analyses from H-Coal waste, from Synthane waste, and a typical coke oven liquor are shown. The coke oven liquor analysis is not from Bethlehem Steel because it was not given in Reference 23. The analysis of the Synthane wastewater is from a parallel publication.

TABLE 5-2 ANALYSES OF WATERS FOR BIOKINETIC DATA

	Typical Coke[39] Oven Liquor	H-Coal[25] Wastewater	Synthane[38] Wastewater
BOD	4,000 - 6,000	1,900 - 2,600	-
COD	7,000	3,100 - 4,200	5,700
Phenol	2,000	750 - 1,500	1,200

In the examples we will show the effect that these different sets of constants have on the size of the aeration basin. It is preferable that the water from a given plant be tested. Lacking tests, Set No. 3 can be used for gas plants and Set No. 2 for liquifaction plants.

5.1.3 The Flow Scheme. Activated sludge processes include the two major components shown in Figure 5-1, the bioreactor followed by the solids separator. These components should be considered an integral system in terms of treatment performance, design and operation of the system.

Certain features of the flow scheme in Figure 5-1 affect the design equations and require discussion before these equations are given. The first feature is that the removal of waste is assumed to be accomplished in the bioreactor only, and the solids separator is assumed to have no effect on the effluent quality S_1. These assumptions may well be valid if the waste concentration is measured as specific soluble compounds such as phenol. However, if certain gross parameters like total BOD or TOC (dissolved plus suspended forms) are used as the measure of efficiency, the effect of the solids separator will have to be considered. Efficiency is defined as:

$$E = \frac{100(S_o - S_1)}{S_o} \qquad (4)$$

where S_o = influent waste concentration, mass/volume

S_1 = effluent waste concentration, mass/volume

The concentration of biological solids in the effluent is a function of their settling properties and the design and operation of the solids separator. Any release of biological solids in the effluent would tend to reduce E as measured by gross parameters. For coal conversion wastewaters it is assumed that the major pollutants will be soluble organics and that the release of biological solids will be minimized and insignificant. Therefore the conditions depicted in Figure 5-1 will be applied in the following discussions.

The remaining features of the flow scheme are:

The bioreactor is completely mixed

There are no active biological solids in the raw waste entering the bioreactor

The total active biological solids in the system equals the biological mass in the bioreactor.

The design and control equations developed in the following sections are specific to the flow diagram of Figure 5-1.

5.1.4 Relationships for the Mean Cell Residence Time. The best parameter for the design and operation of an activated sludge process is probably the mean cell residence time θ_c, which is defined as:

$$\theta_c \equiv \frac{X_T}{(\Delta X/\Delta t)_T} \qquad (5)$$

in which X_T = total active microbial mass in the treatment system, mass; and $(\Delta X/\Delta t)_T$ = total quantity of active microbial mass withdrawn daily, including those solids purposely wasted as well as those lost in the effluent, mass/time. In essence, θ_c is a measure of the average retention time of active microoorganisms in the treatment system, and we will show that a desired treatment efficiency, E, can be obtained by controlling θ_c. Furthermore, θ_c is readily measurable and easily controlled in the operation of an activated sludge process.

One particular value of θ_c, θ_c^m, is of major concern in the design and operation of activated sludge process. θ_c^m represents the minimum θ_c at which a complete failure of the biological process will occur. Below θ_c^m, the organisms are removed from the system at a rate greater than their synthesis rate so that eventually no organisms will be left in the system. θ_c^d, the θ_c value to be used for design, must be significantly greater than θ_c^m. The ratio (θ_c^d/θ_c^m) gives the safety factor for the system. The evaluation of θ_c and θ_c^m will now be made for the flow scheme in Figure 5-1. For this system, θ_c, as defined in Equation (5) is:

$$\theta_c = \frac{VX}{wX_r + QX_e} \tag{6}$$

in which the various symbols are defined in Figure 5-1. Usually the value of X_e may be assumed to be negligible, and Equation (5) then leads to:

$$\theta_c \simeq \frac{V}{w}\frac{X}{X_r} \tag{7}$$

A mat^rial balance for microbial mass around the entire AAS system gives:

(net rate of change of microbial mass) = (growth rate)
- (washout rate)

that is,

$$\left(\frac{dx}{dt}\right)(V) = [Y\left(\frac{dS}{dt}\right) - k_d X]\,V - (wX_r + QX_e) \tag{8}$$

Under steady state, $\left(\frac{dx}{dt}\right)$ will be equal to zero, and substituting for $(wX_r + QX_e)$ from Equation (6) will lead to a relationship between θ_c and substrate utilization rate:

$$\frac{1}{\theta_c} = \frac{Y\left(\frac{dS}{dt}\right)}{X} - k_d \tag{9}$$

Substituting for $\frac{dS}{dt}$ from Equation (3) results in a relationship between θ_c and effluent substrate concentration S_1:

$$\frac{1}{\theta_c} = \frac{YkS_1}{K_s + S_1} - k_d \tag{10}$$

or

$$S_1 = \frac{K_s(k_d + 1/\theta_c)}{Yk - k_d - 1/\theta_c} = \frac{K_s(1 + k_d\theta_c)}{\theta_c(Yk - k_d) - 1} \tag{11}$$

Equation (9) may also be written as:

$$\frac{1}{\theta_c} = Y\ (F/M) - k_d \tag{12}$$

in which F/M is food to microorganism ratio usually in lbs substrate per lb biological solids per day.

Equation (11) shows how control of θ_c controls the effluent concentration S_1 and that as θ_c is reduced, S_1 increases, and if θ_c is made small enough, then S_1 will equal S_o and the process will fail. Thus the value of θ_c^m may be obtained by setting $S_1 = S_o$ in Equation (10):

$$\frac{1}{\theta_c^m} = \frac{YkS_o}{K_s + S_o} - k_d \tag{13}$$

when $S_o >> K_s$, a limiting value of θ_c^m is:

$$(\theta_c^m)\ \text{lim.} = (Yk - k_d)^{-1} \tag{14}$$

Given the values of Y, k, K_s, k_d and S_o, then θ_c^m may be calculated by using Equation (13) or Equation (14). The calculated value of θ_c^m represents the lower bound of θ_c allowable for operation. The actual value of θ_c preferably should be more than twice θ_c^m if adequate control is to be achieved.

There is a second lower limit to θ_c. The sludge residence time must be more than the hydraulic residence time or there will be no recycle of sludge and no control. This limit is important and it is further discussed with numerical examples.

In fact, there is an upper bound to θ_c. The settling characteristics of activated sludge get worse when θ_c is greater than about fifteen days[10]. Although it might appear theoretically possible to use very large values of θ_c and to compensate by using large solids separators, this usually leads to inoperable solids separators and is not practiced. θ_c is usually controlled somewhere between $2\theta_c^m$ and 15 days. However, the upper bound of θ_c may be somewhat higher than 15 days for pure oxygen activated sludge[28], probably because of the improved settling properties of the biological flocs. The preferred limit of 15 days is based on municipal, not industrial, experience. In fact, one set of biokinetic constants that might apply to coal conversion waste force mean cell residence times of up to 70 days or more.

5.1.5 Sludge Recycle. A material balance for microbial mass around the solids separator gives:

$$(Q + q + w)X = (q + w)X_r + QX_e \qquad (15)$$

Assuming X_e to be negligible, that is, perfect solids capture by the separator, and letting $\frac{q}{Q} = r$, the recycle ratio, Equation (15) gives:

$$X = X_r \left(\frac{r + w/Q}{1 + r + w/Q}\right) \qquad (16)$$

or,

$$r = \frac{1 - \frac{w}{Q}\left(\frac{X_r}{X} - 1\right)}{\frac{X_r}{X} - 1} = \text{(using Equation 7)}$$

$$\frac{1 - \frac{V}{Q\theta_c}\left(1 - \frac{X}{X_r}\right)}{\frac{X_r}{X} - 1} \qquad (17)$$

Equations (16) and (17) can also be derived by a material balance for microbial mass around the bioractor alone.

5.1.6 Aeration Basin Volume. Under steady state conditions the rate of substrate utilization by microorganisms, $\frac{dS}{dt}$, may be related to the actual substrate removal as follows:

$$\frac{dS}{dt} = \frac{Q(S_o - S_1)}{V} \tag{18}$$

Incorporating Equation (18) into Equation (9) leads to:

$$\frac{1}{\theta_c} + k_d = \frac{1 + k_d\theta_c}{\theta_c} = \frac{Y}{X}\,\frac{Q(S_o - S_1)}{V}$$

and

$$XV = \frac{YQ\theta_c(S_o - S_1)}{1 + k_d\theta_c} \tag{19}$$

In an operating system, Equation (19) is a relationship between θ_c and X. For the designer, Equation (19) allows determination of the aeration basin volume if X is chosen.

The microbial concentration X is usually expressed as mixed liquor volatile suspended solids (MLVSS) in mg/l. The value of X cannot be chosen arbitrarily since there are practical constraints due to the requirements for oxygen transfer and liquid-solid separation. For air activated sludge systems, X is generally within the range of 1,500 to 5,000 mg/l. The upper bound of X is higher for high purity oxygen systems.

5.1.7 Summary of Aeration Basin Equations.

To design a process the designer is given the influent concentration, S_o, and the feed rate, Q. Preferably there exist reasonable estimates of the biokinetic constants k, k_d, K_s and Y. The minimum value of the mean cell residence time can be calculated from Equation (13):

$$\frac{1}{\theta_c^m} = \frac{YkS_o}{K_s + S_o} - k_d$$

For a series of values of the mean cell residence time, θ_c, the following can be calculated; the effluent concentration from Equation (11):

$$S_1 = \frac{K_s(1 + k_d\theta_c)}{\theta_c(Yk - k_d) - 1}$$

the aeration basin volume for a series of chosen values of MLSS from Equation (19):

$$XV = \frac{YQ\theta_c(S_o - S_1)}{1 + k_d\,\theta_c}$$

the recycle ratio, for which an experimentally determined value of recycle concentration is required, from Equation (17):

$$r = \frac{1 - \frac{V}{Q\theta_c}\left(1 - \frac{X}{X_r}\right)}{\frac{X_r}{X} - 1}$$

the flow rate of waste sludge, w, and the waste sludge production rate, P_x, from Equations (7) and (20):

$$w = \frac{V}{\theta_c} \quad \frac{X}{X_r}$$

$$P_x = \frac{XV}{\theta_c} \tag{20}$$

If biokinetic data are lacking, they can be estimated from experience on related wastes. In an extreme case of lack of information, the aeration basin must be sized on some such criterion as hydraulic residence time, but this is unreliable.

The designer has two variables at his disposal, the mean cell residence time, θ_c, and the mixed liquor suspended solids concentration, X. θ_c must be greater than the minimum value, θ_c^m, must be greater than the hydraulic residence time, and must be long enough to give an acceptable effluent concentrating S_1. The chose value of X may affect the recycle sludge concentration, X_r, and therefore the recycle rate. Both θ_c and X affect the aeration basin volume and the clarifier volume. The final choice, preferably made on cost, requires an understanding of the clarifier. We return to this summary in the following section on solid-liquid separation.

5.1.8 Example 1. Aeration Basin Volume for Moderate Strength Wastewater

Calculations were made for a demonstration size (50×10^6 scf/day) pipeline gas plant having a wastewater flow of 0.3×10^6 gal/day with 2,500 mg BOD/l (which could be a Hygas plant using an eastern coal). The sequence of equations listed above were used with the three sets of biokinetic coefficients from Table 5-1. The recycle sludge concentration was taken from Equation (37), $X_r = 3.4X$. The results are shown in Table 5-3. If the biokinetic constants for coke oven liquor, Set No. 1, were correct, a low value of effluent BOD, S_1, could be obtained for modest values of mean cell residence time (for example, $\theta_c = 10$ days) in an aeration vessel of about 0.2×10^6 gallons.

Calculations based on Set No. 2, for H-Coal wastewater, are presented next. In changing constants we have more than doubled the production rate of sludge (Y increased from 0.2 to 0.48) and very much decreased its decay rate (k_d decreased from 0.17 to 0.02). At the same time the rate of oxidation of BOD has decreased (k decreased from 1.8 to 0.3). The lower oxidation rate will mean a larger aeration basin and the higher sludge production rate will mean that the waste sludge flow rate, w, must be large or operation must be at large sludge concentrations, X.

Because this is a gas plant, we suggest using biokinetic Set No. 3, for Synthane wastewater. The aeration basin would be 0.8×10^6 gals (107,000 ft^3). The system could be operated at a mixed liquor suspended solids concentration, X, between about 3,600 and 4,000 mg/l and a mean cell residence time, θ_c, between about 12 and 20 days. The recycle pipes and pumps should be designed for a ratio of 0.38 ($0.38 \times 0.3 \times 10^6 = 114{,}000$ gals/day = 79 gals/min). The waste sludge pipes and pumps should be designed for 0.026×10^6 gals/day = 18 gals/min. The dry weight of waste sludge is equal to

$$wX_r = \frac{VX}{\theta_c}$$

The maximum expected rate is about

$$0.8\ (10^6 \text{ gals}) \times 8.33 \text{ lb/gal} \times 4{,}000 \text{ ppm} \div 12 \text{ days} = 2{,}200 \text{ lb/day}$$

TABLE 5-3 CALCULATIONS ON AN AIR ACTIVATED SLUDGE PLANT, EXAMPLE 1

FEED 0.3 X 10^6 GAL/DAY AT 2,500 MG BOD/L.

Biokinetic Constants Set No. 1, Coke Oven Liquor, $\theta_c^m = 5.3$ days

θ_c	S_1	V (10^6 gals)			r			w (10^6 gals/day)		
(days)	(mg/l)	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000
10	1.02	0.28	0.19	0.14	0.39	0.40	0.40	0.0082	0.0054	0.0041
12	0.81	0.30	0.20	0.15	0.39	0.40	0.41	0.0073	0.0048	0.0036
15	0.65	0.32	0.21	0.16	0.40	0.40	0.41	0.0062	0.0041	0.0031

Biokinetic Constants Set No. 2, H-Coal, $\theta_c^m = 8.9$ days

θ_c	S_1	V (10^6 gals)			r			w (10^6 gals/day)		
(days)	(mg/l)	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000
15	61	1.82	1.21	0.91	0.30	0.34	0.36	0.036	0.024	0.018
20	38	2.22	1.48	1.11	0.31	0.34	0.36	0.033	0.022	0.016
25	28	2.54	1.69	1.27	0.32	0.35	0.37	0.020	0.030	0.015

Biokinetic Constants Set No. 3, Synthane, $\theta_c^m = 3.3$ days

θ_c	S_1	V (10^6 gals)			r			w (10^6 gals/day)		
(days)	(mg/l)	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000
10	149	0.98	0.65	0.49	0.32	0.35	0.37	0.029	0.019	0.014
12	122	1.13	0.76	0.57	0.32	0.35	0.37	0.028	0.019	0.014
15	98	1.34	0.89	0.67	0.33	0.36	0.37	0.026	0.017	0.013
20	77	1.62	1.08	0.81	0.34	0.36	0.38	0.024	0.016	0.012
25	65	1.85	1.23	0.93	0.34	0.37	0.38	0.022	0.014	0.011

5.1.9 Example 2. Aeration Basin Volume for High Strength Wastewater

These calculations were made for a demonstration size (50×10^6 scf/day) pipeline gas plant having a wastewater flow of 0.17×10^6 gals/day at 18,000 mg BOD/l (which could be a Hygas plant using a Montana coal). In Table 5-4 we have shown the hydraulic liquid residence time calculated from

$$t_{liq} = V/(Q + w + rq) \tag{21}$$

This is a very concentrated waste and alternative procedures to remove organic contamination, such as solvent extraction or resin absorption, should be considered. With the slower kinetics of Set Nos. 2 and 3, large hydraulic residence times are needed to degrade the waste. Attempts to design for moderate mean cell residence times result mathematically in negative recycles when the cell residence time is less than the hydraulic residence time.

Assuming again that Set No. 3 for Synthane wastewater is taken to be correct, the aeration basin would be 4.6×10^6 gallons (615,000 ft^3) and operation could be for X between 3,000 and 4,000 mg/l, θ_c between 20 and 35 days with a 19-day hydraulic residence time. This means a large basin and we suggest that alternatives to biotreatment be considered. The recycle ratio may reach 0.2; recycle flow up to 34,000 gals/day = 24 gals/min. The waste sludge rate may reach 70,000 gals/day = 49 gals/min; the dry waste sludge rate may reach 7,700 lb/day.

5.1.10 Multistage Aeration Basins

An aeration basin may or may not be well mixed. In a well mixed basin the concentrations are those of the effluent. In the feed water if the contaminant concentrations exceed the toxic level, then good mixing is required. For other situations an approach to plug flow or the use of multistages can be advantageous. The rate of disappearance of contaminant substrate was given by Equation (3):

$$\frac{1}{X}\frac{dS}{dt} = \frac{kS}{K_s+S}$$

When S is much greater than K_s, the reaction rate is independent of S. This is a zero order reaction and the rate is the same whether the reactor

TABLE 5-4 CALCULATION ON AN AIR ACTIVATED SLUDGE PLANT, EXAMPLE 2

Feed 0.17 x 10^6 gal/day at 18,000 mg BOD/l.

Biokinetics Set No. 1, Coke Oven Liquor, θ_c^m = 5-9 days

		V(10^6 gals)			r			w(10^6 gals/day)			Liquid Residence Time (days)		
θ_c (days)	S_1 (mg/l)	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000
10	1.02	1.13	0.76	0.57	0.22	0.29	0.32	0.033	0.022	0.017	4.7	3.1	2.4
15	0.65	1.29	0.86	0.65	0.26	0.32	0.35	0.025	0.017	0.013	5.4	3.6	2.7
20	0.53	1.39	0.93	0.70	0.30	0.34	0.36	0.020	0.014	0.010	5.8	3.8	2.9

Biokinestics Set No. 2, H-Coal, θ_c^m = 9.1 days

		V(10^6 gals)			r			w(10^6 gals/day)			Liquid Residence Time (days)		
θ_c (days)	S_1 (mg/l)	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000
15	61	7.57	5.04	3.79	-0.46	-0.17	-0.02	0.15	0.10	0.07	31	21	16
20	38	9.16	6.11	4.58	-0.376	-0.11	+0.02	0.13	0.09	0.07	38	28	19
35	21	12.52	8.35	6.26	-0.20	+0.004	+0.11	0.11	0.07	0.05	52	35	26
60	14	15.72	10.48	7.86	-0.04	+0.11	+0.19	0.08	0.05	0.04	65	44	33
70	13	16.57	11.04	8.29	+0.007	+0.14	+0.21	0.07	0.05	0.03	69	46	34

Biokinetics Set No. 3, Synthane, θ_c^m = 3.0 days

		V(10^6 gals)			r			w(10^6 gals/day)			Liquid Residence Time (days)		
θ_c (days)	S_1 (mg/l)	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000	X=2,000	3,000	4,000
15	98	5.65	3.77	2.82	-0.23	-0.017	+0.09	0.11	0.07	0.06	23	16	12
20	77	6.79	4.53	3.40	-0.17	+0.025	+0.12	0.11	0.07	0.05	28	19	14
25	65	7.72	5.15	3.86	-0.117	+0.061	+0.15	0.09	0.06	0.05	32	21	16
35	53	9.16	6.11	4.58	-0.04	+0.11	+0.19	0.08	0.05	0.04	38	25	19
45	47	10.2	6.81	5.12	+0.02	0.15	0.27	0.07	0.04	0.03	42	28	21

is plug flow or well mixed. The principle is discussed more fully in standard texts such as Reference 40. If S is comparable to K_s, then the reaction rate depends on S and will be higher when S is larger. A plug flow reactor will accomplish the same conversion in a smaller total volume than a well mixed reactor. Particularly for the biokinetics of the Synthane wastewater, K_s is quite large. Some calculations for Example 1 are given in Table 5-5 for multistages. θ_c must be increased from stage to stage to reduce the effluent BOD, S_1. For low effluent concentrations there is a savings in using two stages.

In at least one published case, it has been experimentally demonstrated that the configuration of tanks-in-series can achieve better performance for activated sludge systems in terms of process stability, reliability and efficiency. These process improvements are attributed to the change in flow pattern and fluid regime provided by the serial staging configuration[44].

This does not necessarily mean that two stages can or should be used. As discussed in Section 6, quite a high BOD is acceptable in cooling water makeup. Of course this increases the trouble and expense of operating the cooling system but it decreases the expense of the biological treatment. Also, it is not always possible to use low values of θ_c to obtain low conversions in the first stage. θ_c must be larger than the hydraulic residence time or a negative recycle of sludge must be used. This means recycling clean water which is possible, but wasteful. In the second example with the concentrated wastewater, calculations for multistages could not be made.

In practice, the aeration basin in Example 1 should be so shaped and mixed as to encourage plug flow. In Example 2, plug flow must be discouraged by the shape and mixing pattern of the aeration basin and the entry and exit points of the water. The wastewater is so concentrated that it is certainly toxic and must be diluted by mixing in the aeration basin. Unless we are quite sure that the biokinetic constants have been accurately measured on the wastewater in question, a second stage does give protection and might be useful in Example 2. A sample calculation for a second stage is shown in Table 5-6. A basin of about 0.1×10^6 gallons = 13,400 ft^3 would suffice, which is 2% of the first stage basin. The recycle ratio is 0.41; 48 gals/min recycle. The waste sludge rate is 0.4 gals/min.

TABLE 5-5 CALCULATIONS ON A MULTISTAGE AIR ACTIVATED SLUDGE PLANT FOR EXAMPLE 1

Feed: 0.3×10^6 gals/day at 2,500 mg/l BOD

Biokinetic constants, Set No. 3, Synthane, $\theta_c^m = 3.3$ days

MLSS: 3,000 mg/l

θ_c (days)	S_o (mg/l)	S_1 mg/l	V (10^6 gals)
One stage			
25	2500	65	1.233
Two stages			
6	2500	312	0.405
25	312	65	0.125
			0.530
Three stages			
5	2500	452	0.325
12	452	122	0.104
25	122	65	0.024
			0.458

TABLE 5-6 SECOND STAGE CALCULATION FOR EXAMPLE NO. 2 USING BIOKINETIC SET NO. 3, SYNTHANE WASTEWATER

Inlet flow, $Q = 0.17 \times 10^6$ gals/day
Inlet BOD, $S_c = 300$ mg/l
MLSS, $X = 3,000$ mg/l

θ_c (days)	S_1 (mg/l)	V (10^6 gals)	r	w (10^6 gals/day)	Liquid Residence Time (days)
20	77	0.056	0.41	0.0008	0.23
35	53	0.084	0.41	0.0007	0.35
70	39	0.116	0.41	0.0005	0.48

5.2. Solid-Liquid Separation

The solid-liquid separator, usually called a clarifier, is a critical and integral part of the activated sludge process. The separator should be designed to satisfy two functions: 1) clarification, which is the production of an overflow relatively free of suspended solids; and 2) thickening, which is the production of an underflow that contains, in sufficiently high concentration, the active biological solids to be returned to the bioreactor.

5.2.1 Clarification

The requirement of clarification has long been the sole basis of clarifier design, and the design criteria are in the form of a hydraulic overflow rate in gallons per day per square feet. The procedure for determining the unit area required for sedimentation involves the measurement of the settling rate of the sludge in question, using the laboratory settling rate procedure. The settling rate expressed in feet per hour can be converted to an overflow rate by means of the following equation:

$$OR = (SR\ \text{ft/hr}) \times 7.45\ \text{gal/ft}^3 \times 24\ \text{hr/day} \qquad (22)$$

where, OR = overflow rate (gallons/day/ft^2)

SR = settling rate (ft/hr)

This overflow rate based on the laboratory settling rate thus determines the maximum overflow rate which can be expected to produce a reasonably clarified effluent. Hydraulic considerations and short-circuiting introduce inefficiencies in the final clarifier which should be accounted for in the design. An adjusted overflow rate can be calculated which will make allowances for these inefficiencies.

$$ORD = K_1 \times OR \qquad (23)$$

where, ORD = design overflow rate (gpd/ft^2)

OR = laboratory overflow rate (gpd/ft^2)

K_1 = a dimensionless correction factor

The magnitude of the constant K_1 is a function of the tank configuration, the inlet and outlet design, and the hydraulic efficiency of the clarifiers.

Although exact measurements of K_1 are not available, the magnitude of this factor ranges from about 0.5 to 0.8 for the various final settlers which are commercially available.

5.2.2 Theory of Thickening

The relationship between thickening and the clarifier design is more complex and was not fully recognized until the early 1970's. (A complete summary to 1972 is given in Reference 24). In Reference 24 it was found that the settling characteristics of municipal plants sludges varied from plant to plant and also varied with time in any one plant. (This variation with time is because municipal plants deal with a wastewater whose characteristics vary with time). Thus, an understanding of thickening requires experiments on the specific wastewater. The following theoretical discussion is intended to help correlate experiments, however, since we know of no experiments on coal conversion wastewater, the theory cannot be used for design at this moment.

Today, final separators must be designed for an arbitrary overflow rate and the concentration of the thickened sludge must be arbitrarily assumed. If the size of the separator required to give the desired degree of thickening exceeds the size required for clarification, the thickening function controls the sizing of the separator. Conversely, if the clarification requirement is larger, the clarification controls. The hydraulic overflow rate should be determined for both clarification and thickening, and the larger clarifier should be used.

The theory of solids separation for thickening has been well documented[7-10]. The rate of solids transport to the bottom of the separator, M, in pounds of solids per unit time, is directly proportional to the cross-sectional area of the separator, A, and the rate at which solids reach the bottom of the separator per unit area; that is, the solids flux G, commonly in pounds per square foot per day:

$$G = M/A \qquad (24)$$

Generally there will be a limiting solids flux, G_L, whose value depends on the solids settling characteristics and other parameters, and on a solids loading rate, M_a, being applied to the separator. The goal of design is to provide an adequate area A so that the applied solids flux:

$$G_a = G_L = \frac{M_a}{A} = \frac{(Q + q + w)X}{A} = \frac{Q(1 + r + w/Q)X}{A} \qquad (25)$$

If the area is inadequate and the applied solids flux, G_a, becomes larger than G_L, then the solids tend to build up and are eventually lost through the overflow. This will cause the effluent water quality to deteriorate. On the other hand, if a more than adequate area is provided, then G_a is less than G_L and the functions of thickening and clarification may be simultaneously satisfied. If anaerobic denitrification can be avoided in the separator by a quick withdrawal of the concentrated sludge, an overdesign of the separator should have no detrimental impact except for its higher cost.

To evaluate G_L, a general expression for G is needed. Qualitatively the solids are transported to the bottom of the separator by two mechanisms: gravitational subsidence, and the bulk downward transport due to sludge withdrawal from the bottom of the separator. The total solids flux at which solids of concentration X_i pass downward in the separator is:

$$G = X_iV_i + X_iU \qquad (26)$$

in which V_i is the settling velocity of the solids at concentration X_i, and U is the average downward velocity due to the removal of sludge at concentration X_r, the solids concentration being returned to the bioreactor. The value of U depends on the flow rate of recycled and wasted sludge, q + w, and A, so:

$$U = \frac{q + w}{A} = \frac{rQ + w}{A} \qquad (27)$$

The value of V_i is a function of the solids concentration, C_i, and a commonly accepted expression for V_i is:

$$V_i = aC_i^{-n} \qquad (28)$$

in which a and n are empirical coefficients. Larger values of a represent sludges settling well. Larger values of n represent sludges with settling properties very sensitive to changes in C (n is greater than one). If no inert solids are applied to the separator, then C_i is equal to X_i, the biological solids concentration or MLSS. Since coal gasification wastes contain primarily soluble organics and little inert solids:

$$V_i = aX_i^{-n} \qquad (29)$$

A typical relation between V_i and X_i is shown in Figure 5-4.

Substitution of Equations (27) and (28) into Equation (26) gives:

$$G = aX_i^{(1-n)} + \frac{rQ + w}{A} X_i \qquad (30)$$

A typical graphical presentation of Equation (30) is shown in Figure 5-5. Equation (30) is not applicable for very small values of X_i because the first term, $aX_i^{(1-n)}$, goes to infinity when $n > 1$. On Figure 5-5 the actual curves are shown with dashed lines for small X_i. The total flux is shown as the sum of its components, X_iV_i and X_iU, and there will be a minimum which acts as the limiting solids flux, G_L, with a corresponding solids concentration of X_L. The lower solids flux when X_i is less than X_m is of no practical concern because the MLSS in the influent to the solids separator is usually larger than X_m and less than X_L. To reach the returned solids concentration, X_r, the solids concentration in the separator will have to pass through X_L and, thus, G_L becomes the maximum solids flux which can be transported through the bottom of the solids separator.

In Figure 5-5 we find that X_L corresponds to the value of X_i when:

$$\frac{\partial G}{\partial X_i} = 0 \text{ and } \frac{\partial^2 G}{\partial X_i^2} > 0$$

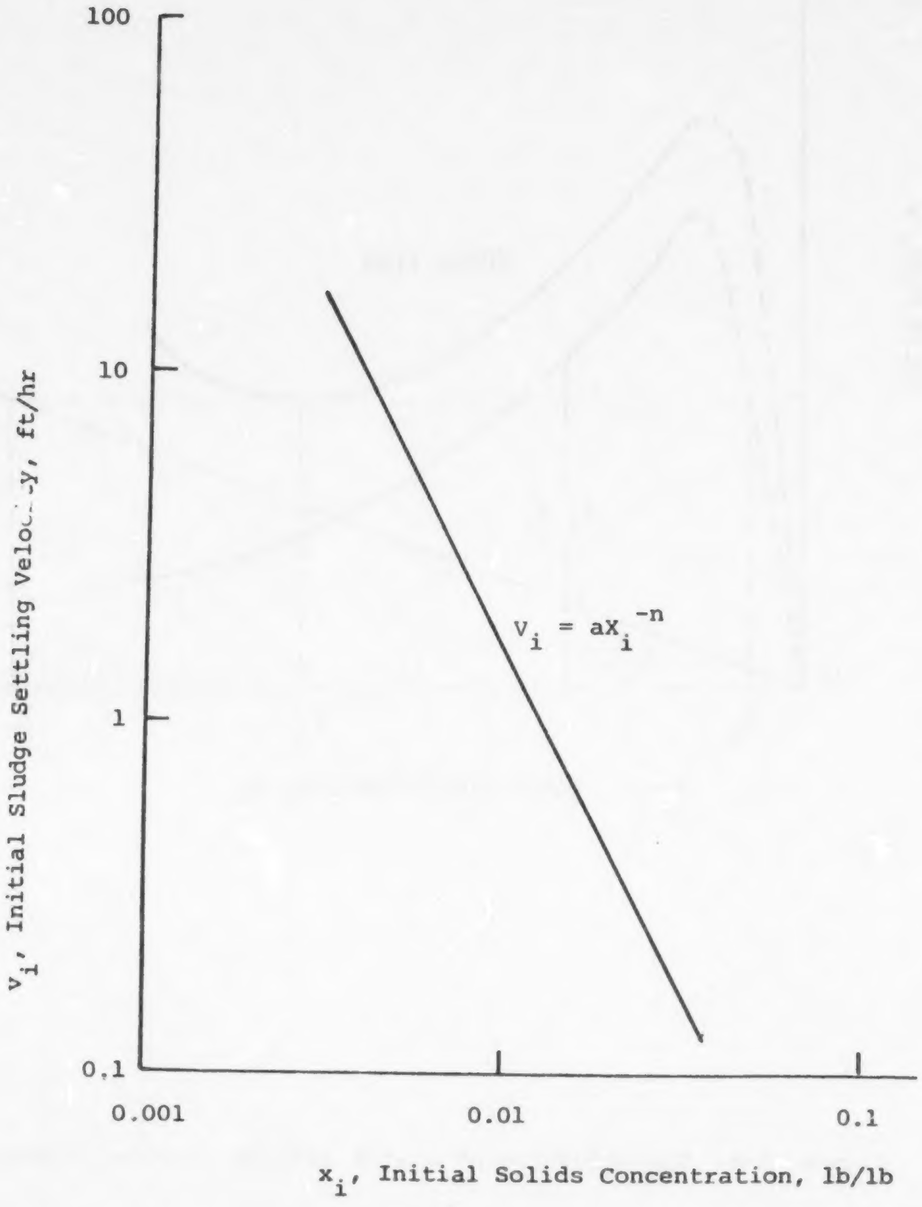


Figure 5-4. Typical settling velocity vs. solids concentration.

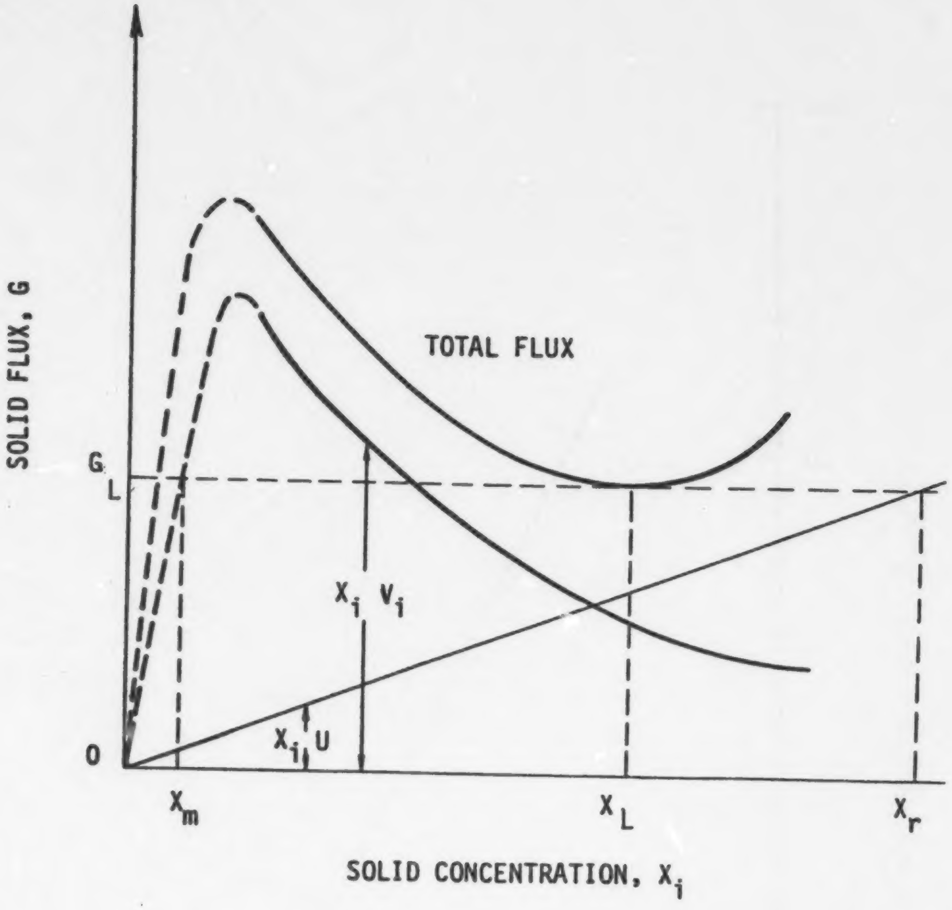


Figure 5-5. Typical curve of solids flux vs. solids concentration.

Differentiation of Equation (30) gives:

$$\frac{\partial G}{\partial X_i} = a(1-n)X_i^{-n} + \frac{rQ + w}{A} \tag{31}$$

and by setting the righthand side of Equation (31) equal to zero, X_L can be determined as:

$$X_L = \left[\frac{a(n-1)A}{rQ + w}\right]^{1/n} \tag{32}$$

Differentiation of Equation (31) gives:

$$\frac{\partial^2 G}{\partial X_i^2} = \frac{an(n-1)}{X_i^{n+1}} \tag{33}$$

As long as n > 1:

$$\frac{\partial^2 G}{\partial X_i^2} > 0$$

and Equation (32) gives the X_L corresponding to G_L. Substituting Equation (32) into Equation (30):

$$G_L = \left\{a(n-1)\right\}^{1/n} \left(\frac{n}{n-1}\right) \left(\frac{rQ + w}{A}\right)^{(n-1)/n} \tag{34}$$

The hydraulic overflow rate required to satisfy the thickening function can be obtained by equating G_L from Equations (34) and (25) to obtain:

$$\frac{Q}{A} = \frac{a(n-1)\left(\frac{n}{n-1}\right)^{n}(r + w/Q)^{n-1}}{X^{n}\,(1+r+w/Q)^{n}} \qquad (35)$$

or, since $(Q + q + w)X = (q + w)X_r$

that is $(Q + rQ + w)X = (rQ + w)X_r$

$$\frac{Q}{A} = \frac{a(n-1)\left(\frac{n}{n-1}\right)^{n}}{X_r^{\,n}(r+w/Q)} \qquad (36)$$

5.2.3 Continuation of Summary of Design Equations

Equation (35) or (36) can be used to find the thickener area, A. In these equations the terms, a and n, are experimentally determined constants in the settling Equation (29). The mixed liquor suspended solids concentration, X, is set by design. The feed rate, Q, is given. The recycle ratio, r, and the wasted sludge rate, w, are from the equations for the aeration basin previously given. The return sludge concentration, X_r, is experimentally determined; it cannot be found from Equations (35) and (36) because they are not independent equations.

Adequate clarification of the effluent water is also required. If the area of the clarifier determined from the equations above does not give satisfactory water, then the area must be made bigger according to the clarification requirement.

Equation (35) or (36) must, of course, be used with the design equations for the aeration basin previously given; in particular with Equation (17) which relates the recycle ratio, r, to the recycle concentration, X_r. If the dependence of X_r on Q/A is known, it will be necessary to iterate between Equations (17) and (35) until a consistent set of values for X_r, r and Q/A is found.

At this point it begins to be possible to estimate the cost of the system for chosen values of θ_c and X. The cost of the aeration basin is not so easy to determine because it is not just a function of volume, but depends also on shape, which is controlled by choice of aeration equipment (discussed in the next section). At first a simplified cost estimate dependent only on volume will be used. The cost of the clarifier is mostly a function of the area. In general, a larger X will mean a smaller aeration basin (but not a smaller oxygen requirement) and a larger clarifier. A minimum cost value for X can, in theory, be found. We must say that experimental information to do such a perfect design is seldom available.

5.2.4 Values of the Thickening Constants

We have found no published results for thickening sludges from the biological oxidation of coal conversion plant wastewater. One piece of information has been reported for coke oven liquor[23], namely

$$\frac{X_r}{X} = 3.4 \tag{37}$$

This particular point was measured at X = 2,600 mg/l. Until better information is available, Equation (37) should be used for air systems. For oxygen, Union Carbide has suggested that X_r = 20,000 mg/l.

Also, until settling rates have been measured, an arbitrary overflow rate should be used to find the area of the solids separator. The coke oven liquor[23] was clarified satisfactorily at 685 gal/(day)(ft^2). For an H-Coal wastewater a design overflow of 560 gal/(day)(ft^2) has been used[25]. For municipal plants the Ten States Standards call for an overflow rate of 600-800 gal/(day)(ft^2), but this may be too high for coal conversion waste. Until better information is available, we suggest sizing final clarifiers for safety at 400-500 gal/(day)(ft^2). If an intermediate clarifier is used, it can be sized at 600-800 gal/(day)(ft^2). These rates are applicable whether air or oxygen is used.

5.2.5 Sludge Dewatering

Sludge dewatering is a big job in these plants. Available experience is all on municipal waste and often when the sludge is partly primary and partly secondary. In our example the sludge is entirely secondary and need not have the same dewatering characteristics. For many municipal secondary sludges the dewatering rate on a vacuum filter is dependent on feed concentration and the use of a dissolved air flotation thickener which can multiply the sludge concentration about 2 to 2.5 times is justified. We do not know if a thickener is justified for this sludge.

Filters require attention. One has the choice of using a small filter, a small sludge holding basin, a lot of operating labor and some standby equipment or, on the other hand, a large filter, a large sludge holding basin, a little operating labor and no standby equipment. A comparison is given in the following example. We suggest sizing the filter for 3 lb dry weight/(ft^2)(hr) = 72 lb dry weight/(ft^2)(day).

5.2.6 Continuation of Examples

Example 1. A flow diagram is given in Figure 5-6. The clarifier will be sized for 424 gals/(day)(ft^2) and have a 30 ft diameter and 707 ft^2 area. The dry sludge production rate may reach 2,200 lb/day. Assuming that a filter is operated 7 hrs/day every day of the week at 3 lb dry weight/(ft^2)(hr), the active filter area must be 105 ft^2. A rotary filter of 6 ft diameter and 8 ft long has adequate active area. A 24-hour sludge holding basin must be provided. The liquid volume is 0.026×10^6 gallons = 3,500 ft^3. To avoid having the sludge set-up in the basin, stirring is necessary. The recycle flow passing through the basin may supply adequate stirring. A clarifier mechanism is often used.

Example 2. This flow diagram is given in Figure 5-7. Two stages are shown as discussed under Multistage Aeration Basins. The first clarifier will be 18 ft diameter, 254 ft^2, 668 gals/(day)(ft^2). The second clarifier will be 22 ft diameter, 380 ft^2, 447 gals/(day)(ft^2).

The dry sludge rate is large and can reach 7,700 lb/day. The following options are typical of those that can be considered:

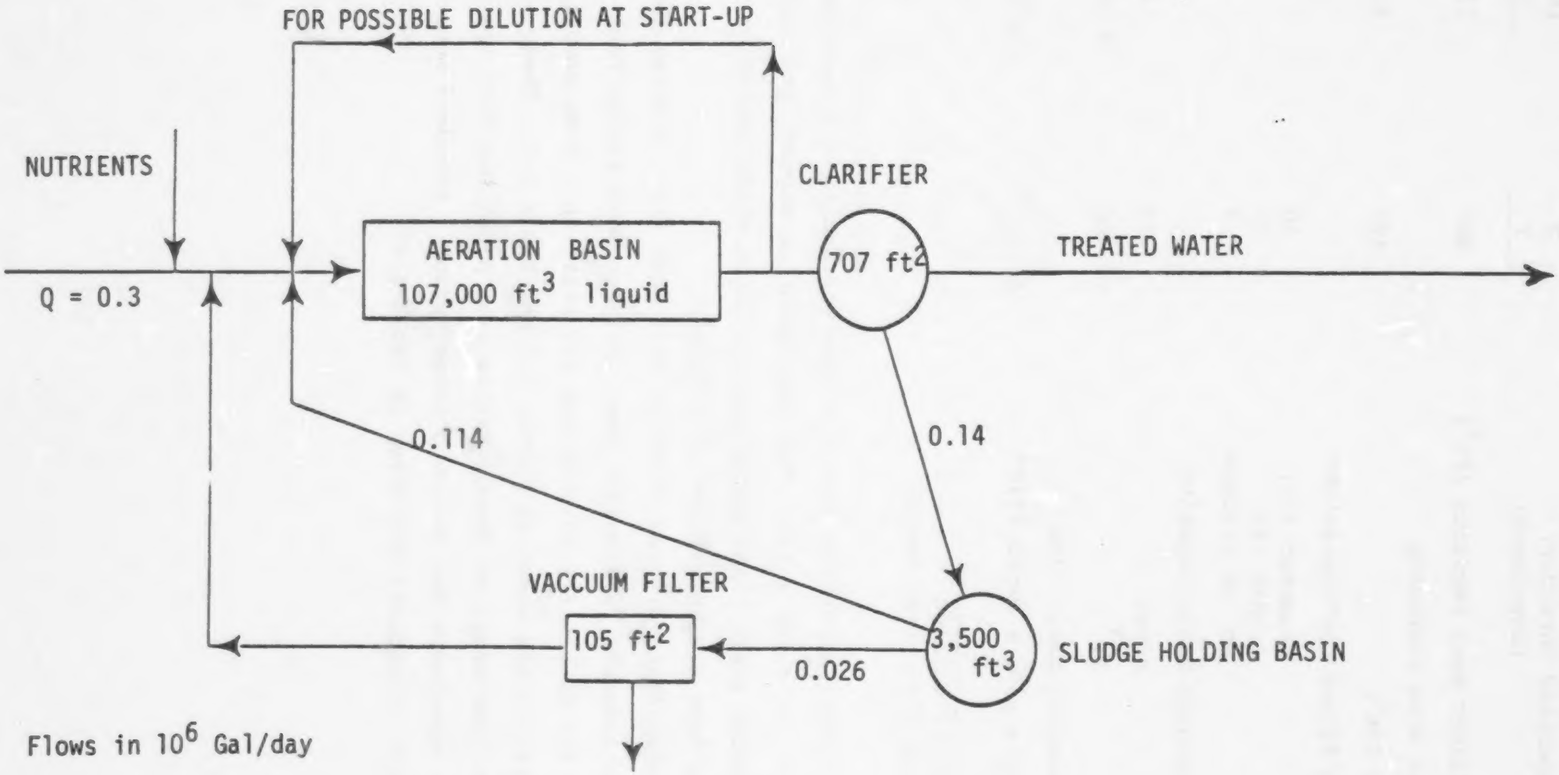

FOR POSSIBLE DILUTION AT START-UP
NUTRIENTS
CLARIFIER
AERATION BASIN
107,000 ft^3 liquid
707 ft^2
TREATED WATER
Q = 0.3
0.114
0.14
VACCUUM FILTER
105 ft^2
3,500 ft^3
SLUDGE HOLDING BASIN
0.026
Flows in 10^6 Gal/day

Figure 5-6. Flow diagram for Plant Example 1. - Moderate strength wastewater.

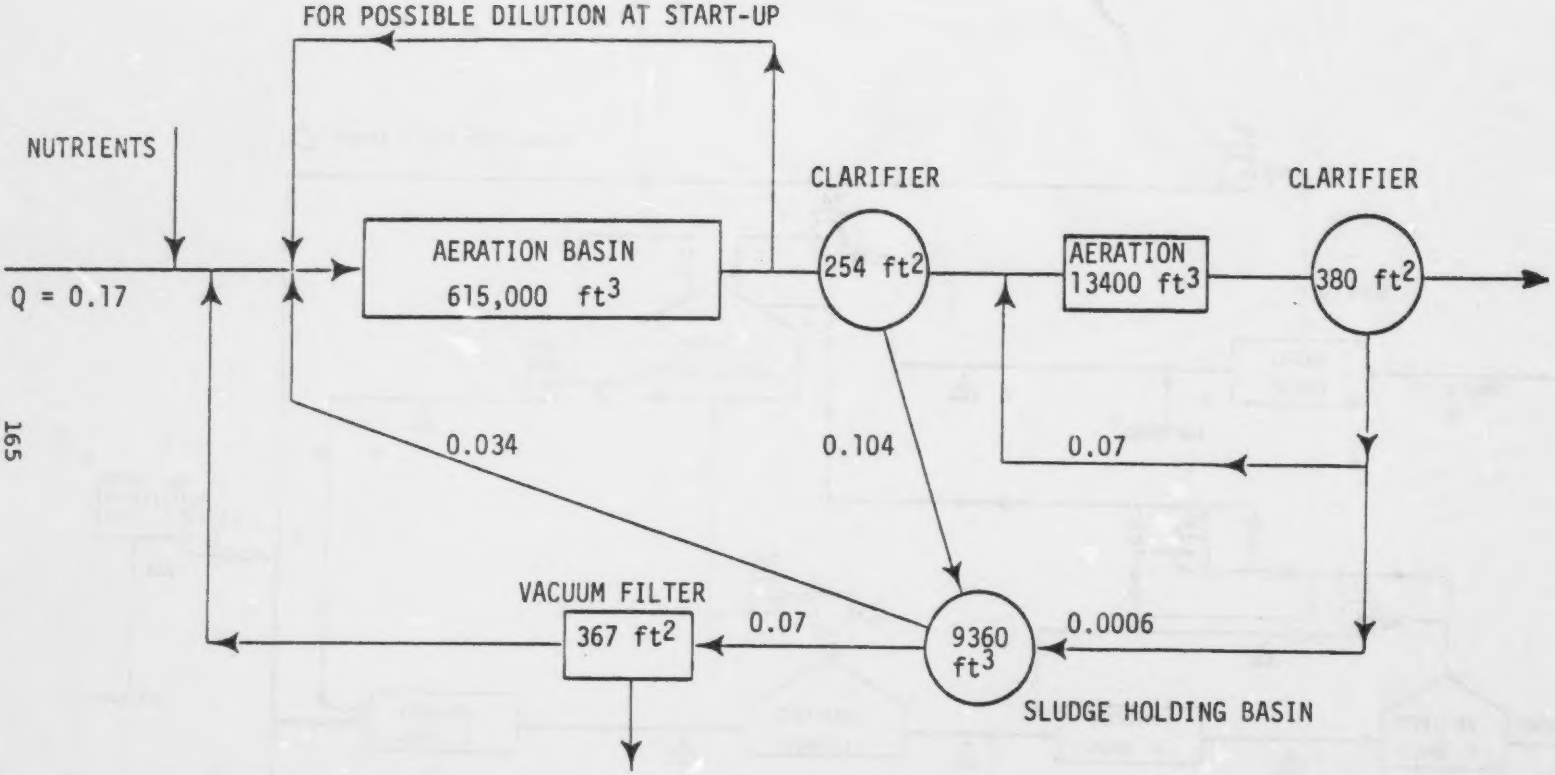
Filter operated (hrs/day)	7	15	24
(days/week)	7	7	7
Active filter area required (ft^2)	367	171	107
Installed area including standby (ft^2)	372	302	216
Possible filter configuration*			
diameter (ft)	10	6	6
length (ft)	12	8	6
no. of filters	1	2	2
Sludge holding basin capacity			
hours	24	24	12
ft^3	9,360	9,360	4,680
Sludge holding basin size			
side x side x depth(ft)**	34x34x10	34x34x10	24x24x10

---

*From Ametek catalog
**Includes 2 ft. free board

Two shift operation does not seem worthwhile and the choice is between one shift and three shift. For this plant we suggest one shift operation. A commercial scale plant would require three shift operation. Operation for five days a week was not considered.

A simplified diagram is shown in Figure 5-8. Gravity flow through the plant is assumed. A transfer pump, P6, can move sludge back and forth between the stages for wasting and for start-up. Some sampling and instrumentation points are shown in Figure 5-8 and Table 5-7. These are more analyses than usual on demonstration size plant and they are intended to provide experience for use on a larger plant. Standard sources of analytical procedures are given in Table 5-8.


FOR POSSIBLE DILUTION AT START-UP
NUTRIENTS
Q = 0.17
AERATION BASIN
615,000 ft^3
CLARIFIER
254 ft^2
AERATION
13400 ft^3
CLARIFIER
380 ft^2
0.034
0.104
0.07
VACUUM FILTER
367 ft^2
0.07
9360
ft^3
0.0006
SLUDGE HOLDING BASIN

Flows in 10^6 Gal/day

Figure 5-7. Flow diagram for Plant Example 2. - High strength wastewater.

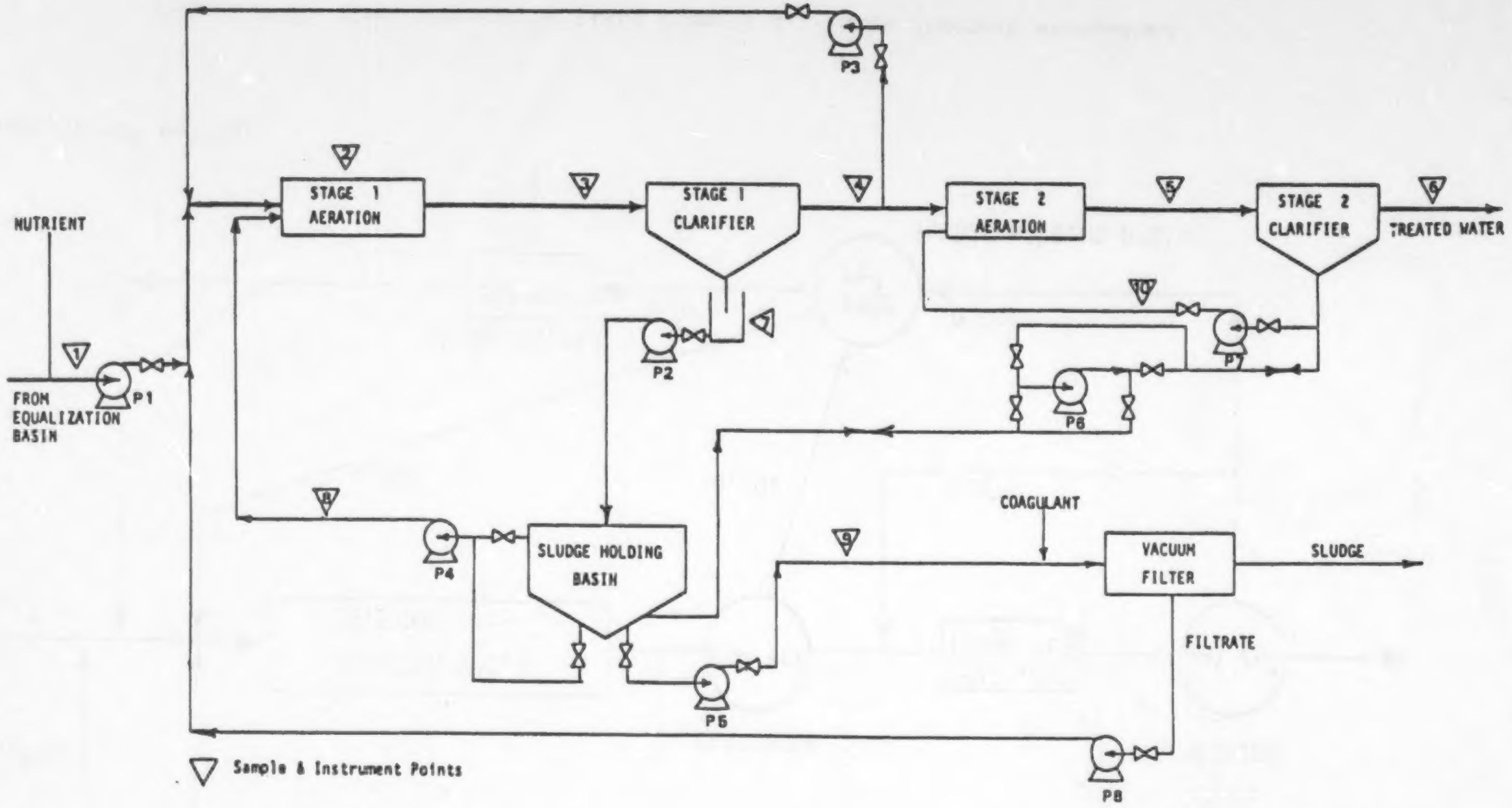

NUTRIENT
1
FROM EQUALIZATION BASIN
P1
2
STAGE 1 AERATION
3
STAGE 1 CLARIFIER
4
P3
STAGE 2 AERATION
5
STAGE 2 CLARIFIER
6
TREATED WATER
7
P2
10
P7
P6
8
P4
SLUDGE HOLDING BASIN
P5
9
COAGULANT
VACUUM FILTER
SLUDGE
FILTRATE
P8
Sample & Instrument Points

Figure 5-8. Simplified process diagram for air activated sludge, Example 2.

TABLE 5-7 SAMPLING AND INSTRUMENTATION POINTS

1	2	3	4	5	6	7	8	9	10
Flow	DO	Flow	Phenol	Flow	Phenol	Flow	Flow	Flow & Totalizer	Flow
Phenol	Temp.	DO	BOD	DO	BOD	SS	SS	SS	SS
BOD	pH	SS	COD	SS	COD		VSS		VSS
COD	SS	Temp.	TOC	Temp.	TOC				
TOC	VSS		SS		SS				
SS									
Temp.									
pH									

TABLE 5-8 SOURCES OF ANALYTICAL PROCEDURES

Analysis	Standard[41] Methods 14th. Ed.	ASTM[43]	EPA[42]
pH	460-465	178-187	239
Alkalinity	278-282	111-119	3-8
Acidity	273-277	111-119	1-2
Specific Conductance	71-75	102-125	275-276
Chloride	302-309	270-275	29-34
Total Dissolved Solids (Filterable)	92-93	188-197	266-267
Suspended Solids (Non-filterable)	94	188-197	268-272
Dissolved Oxygen	440-454	372-377	51-68
BOD	543-550	-	11-12
COD	550-557	473-475	20-28
TOC	532-534	469-472	236-238
Phenol	574-592	553-568	241-248
Ammonia Nitrogen	407-418	237-241	159-174
TKN	437-440	577-579	175-196
Nitrite - N	434-436	366-371	215-216
Nitrate - N	418-433	363-365	197-214
Phosphorous	466-483	388-407	249-265
Calcium	185-191	160-163	19,103-104
Magnesium	221-223	160-163	114-115
Silica	484-492	401-407	274
Sulfate	493-498	429-435	277-283
Turbidity	113-139	222-228	295
Color	64-71	-	36-39
Residual Chlorine	309-345	276-289	35
Coliform	913-942	-	-
Temperature	-	-	286

5.3 Aeration

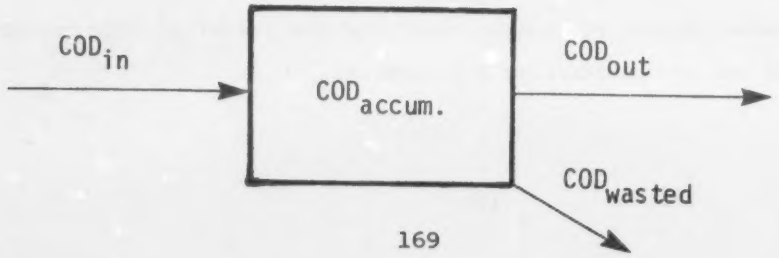
Oxygen must be supplied to maintain the biological oxidation. To be used the oxygen must be dissolved. A dissolved oxygen level of 1.5 to 2 mg/l should be maintained in the aeration basin. We begin by discussing the oxygen required and then the equipment that can be used to cause oxygen from air to dissolve at the desired rate.

5.3.1 Oxygen Requirement. The oxygen requirement, pounds of oxygen required per pound of BOD removed, is a function of F/M and COD/BOD ratios. The effect of COD/BOD ratio may be of particular interest in these waters since the fate of COD in the biological treatment of coal conversion condensates is unknown at present. Ideally, this oxygen requirement should be determined in pilot studies by one of the following methods: measurement of oxygen utilization rate (OUR in mg/l/hr) of the biomass, or total COD balance.

The OUR measurements should be made two or three times per day on the mixed liquor from the bioreactor. The measurement involves the use of a probe to monitor the dissolved oxygen concentration to depletion in a mixed liquor sample. The slope of the straight line section of the curve of dissolved oxygen versus time is taken as the OUR.

Although the OUR measurement is simple to make, the result may be inaccurate because the dissolved oxygen measurement using a probe is not always exact. The inaccuracy may occur particularly with high BOD waters. To make a more precise determination of the oxygen requirement, the COD balance may be used, which is more complex.

The method of total COD balance involves a complete inventory of COD around the biotreatment system, including the bioreactor and solids-liquid separator. The oxygen requirement can be so determined since COD is measured and calculated in oxygen equivalents. For a general situation the COD fluxes around the system can be represented in the following diagram:



where:

COD_{in} = total COD content of the influent to the bioreactor, excluding the recycled sludge;

COD_{out} = total COD content of the effluent from the solids-liquid separator;

COD_{wasted} = total COD content of the wasted sludge;

$COD_{accum.}$ = total COD gained due to MLSS and clarifier solids inventory increases.

The following equation then represents a COD balance around the system:

$$COD_{in} - COD_{out} - COD_{wasted} - COD_{accum.} = \text{oxygen requirement}$$

Theoretically, the $COD_{accum.}$ in this equation will drop out if a true study state can be maintained in the system. However, the MLSS and clarifier solids blanket tend to vary. In actual operation, the total COD will be determined on daily composite samples of influent, effluent, waste sludge and mixed liquor; thus COD_{in}, COD_{out} and COD_{wasted} can be calculated. The total COD determination of mixed liquor and measurement of MLVSS leads to a ratio between COD and MLVSS, which can be used to evaluate $COD_{accum.}$. The COD gained due to clarifier solids increase may be monitored by measuring the thickness of the sludge blanket. One technique to convert the thickness increase to a COD value is to assume half of the thickness increase as having the solids concentration of the return or wasted sludge, and the other half as having the solids concentration of the mixed liquor. The conversion of solids to COD will be achieved by using the COD/MLVSS ratio previously described.

Given the design flow, BOD feed concentration and required BOD removal, the oxygen requirement in pounds of oxygen required per day can be calculated using the ratio between pounds of oxygen required per pound of COD removed, determined above and the corresponding BOD removal.

5.3.2 Values for Oxygen Requirement

We know of no oxygen uptake rates or COD balances done on coal conversion wastewater. When surface aerators were used in the treatment of coke oven liquor[23], it was found that 18.2 lb phenol were removed per day per horsepower. This is about 43 lb BOD removed/(day)(hp) which compares closely with typical values in the literature[5] of 45-50 lb BOD/(day)(hp). Pending additional information, this value must be used if surface aerators are used. For diffused aeration, a true oxygen requirement is needed. Assuming that a surface aerator transfers between 1.8 and 2.6 lb O_2/hp-hr, the figure of 43 lb BOD/(day)(hp) translates to between 1 and 1.4 lb O_2/lb BOD removed. Pending additional information, a figure of 1.3 lb O_2/lb BOD should be used.

5.3.3 Aeration Equipment and Aeration Basin Shape

A variety of equipment is available to mix air and water and to encourage the dissolution of oxygen. A useful classification of the equipment[4,28] includes

1. Surface aerators: These are rotating stirrers near the surface of the water designed either to throw water up in a spray, or to pull air down into a vortex.

2. Turbine mixers: These are rotating stirrers set near the bottom of the water with compressed air released from a pipe just below the stirrer.

3. Diffusion systems: These are spargers set on pipes at the bottom of the aeration basin. If porous pipes are used, fine gas bubbles are obtained. Coarse gas bubbles result when individual spargers are used. The individual spargers are like mushroom caps over the top of open vertical pipes. Individual static mixers are also used and these draw water into the airstream before it is released. In all diffusion systems the only moving machinery is the air compressor which is not in the water.

At this point in the design, the designer knows a required aeration basin volume and a required rate of supply of oxygen. For any chosen piece of equipment supplying oxygen, the energy used and the capital cost will depend on the shape of the aeration basin; on its length, width and depth; whether partition walls are used, and whether tank baffles are used. The basin shape and the aeration equipment must be matched to result in a system with the lowest cost. The value of the number lb O_2/(day)(ft^3 of basin) is not constant for the industry and this means that there is no one preferred type of aeration equipment. Furthermore, all equipment of one type (for example, all surface aerators) is not designed to operate with maximum efficiency in the same basin. Some surface aerators are designed for optimum efficiency in wide, shallow basins; others for deeper, narrower basins with wall baffles. The lengthy process of matching equipment, basin and oxygen requirements cannot be avoided. Manufacturers of aeration equipment are highly competitive and will provide test results together with recommendations of the basin shape preferred with their equipment. Taking into account the cost of the basin, as well as the cost of the aeration equipment, the designer can choose the least costly overall system.

Mixing is an important factor in the design and operation of aeration systems. The purpose of mixing is to uniformly disperse dissolved oxygen and activated sludge throughout the basin, and mixing requirements have been related to the power density in aerator horsepower per unit volume of aeration basin. It has been reported[6] that 0.006 to 0.01 hp/1,000 gal is required to maintain uniform dissolved oxygen, while the minimum hp/1,000 gal to prevent any bottom deposition of activated solids increases with increasing aerator spacing. To maintain a minimum bottom velocity of 0.4-0.5 ft/sec, at least 0.02-0.03 hp/1,000 gal is needed at a distance of 14 ft from the aerator, and 0.05-0.06 hp/1,000 gal at a distance of 35 ft. These minimum power densities may be used as a design guide when no pilot plant data are available with the specific surface aerators to be used. No such general experience has been published on diffusion aerators and the manufacturers must be asked. However, we foresee that the energy needed to dissolve oxygen into coal conversion wastewaters will so far exceed the minimum energy for mixing that mixing will not usually be a limitation.

The following section offers some general opinions on aeration equipment by type, suggests the kind of information that most manufacturers can supply, and shows how to use this information.

Surface Aerators

This type of aerator is often the cheapest, both to buy and to run. Surface aerators also may be the noisiest type, the noise coming from the movement of water. Upflow, or spray type, surface aerators give the most cooling of the water and are the most prone to form aerosols. Maintenance, while not complex, does involve going out on the water. (If the water level must vary in the aeration basin, then pier-mounted surface aerators and turbines should not be used.)

Surface aerators are made for an upflow or a downflow of water. They are made to float or to be mounted on concrete piers. Each type is most efficient in a particular shape of basin. The performance of surface aerators is rated in terms of their oxygenation efficiency as pounds of oxygen per horsepower-hour at standard conditions. Standard conditions refer to a test temperature of 20°C, zero initial dissolved oxygen concentration, and tap water as the test liquid. In addition, oxygenation efficiencies reported by the manufacturers are usually determined by testing a single aerator rather than multiple aerators as usually used in actual treatment. Also, tests are made at a fixed depth, commonly in a basin 10 to 12 feet deep; this depth frequently gives the lowest excavation cost.

To correct the results of the test under standard conditions, the following equation may be used[28]:

$$N = N_o \frac{\beta C_{walt} - C_L}{9.17} (1.024)^{(T-20)} \alpha \qquad (38)$$

where,

N = lb O_2/hp-hr transferred under field conditions

N_o = lb O_2/hp-hr transferred in water at 20°C and zero dissolved oxygen

β = salinity-surface tension correction factor, usually 0.95

C_{walt} = oxygen-saturation concentration for waste at given temperature and altitude

C_L = operating oxygen concentration

T = temperature, °C

α = oxygen-transfer correction factor for waste, usually 0.8 to 0.85 for wastewater

Use of Equation (38) requires information better known to the plant designer than to the aeration equipment manufacturer. The temperature chosen will usually be a hot, summer temperature when oxygen solubility is minimal. C_{walt} applies at the chosen temperature. The constants β and α can be found from tests or taken from experience.

Equation (38) says nothing about the basin shape and each manufacturer should be asked to state the preferred shape. It is particularly important that multiple aerators in the same basin not be so close to each other that they interfere and lose efficiency[5].

Turbine Mixers

Test results and nomographs for designing have been given in Reference 1. Turbine mixers can be useful when a high oxygen rate is required in a small basin, or if very deep basins are to be used; turbines give better mixing than any other type of aerator in such basins.

Diffused Aeration

Fine bubble diffusers can cause the dissolution of about 25% more air than coarse bubble diffusers, but they are easily clogged and maintenance costs can often overcome their inherent advantage. Coarse bubble diffusers (and probably static mixers although less experience is available) have the particular advantage of ease of maintenance. The only moving machinery is the air compressor which is usually inside a building and not on the water. Diffused aeration is particularly useful if dissolved oxygen is to be controlled when the feed is varying[53]. Piping procedures and a description of compressors is fully given in Reference 28. A series of tests on static mixers has been published[35]. Piping is straightforward. Pipes should be large enough that frictional losses are less than one-fifth of the total pressure loss; the main pressure loss equals the depth. Another procedure frequently found to be economical is to allow 2 psi frictional pressure drop. The main header can be sized for about 1,000 ft/sec and the secondary lines for a lower velocity.

Placement of the diffusers and the surface shape of the water affect not only the efficiency of absorbtion, but also the type of mixing that results in the basin. Diffusers are often placed to one side to produce a rolling motion in the mass of water in the basin. The mixing pattern, and therefore placement of the diffusers, can determine whether the basin approaches closer to plug flow or to complete mixing. Plug flow is advantageous with fairly dilute feeds, but good mixing is required with strong feeds to prevent toxic contaminants from killing the system.

An extensive series of tests have shown that placement of the diffusers and basin width affect the absorbtion efficiency[3]. In these cases a narrow basin and a midwidth position are preferred; however, this may not be true for other manufacturers.

There is discussion on just how efficient a diffusion system will be and how this is affected by depth. Certainly the efficiency of a diffusion aeration system increases with increasing depth. The limit is where the basin is so deep that the rising air bubbles cease giving adequate mixing. The deeper the basin, the larger the fraction of the compressed air which dissolves. In a deep basin less air needs to be compressed. The actual relationship depends on the diffuser and can be supplied by the manufacturer. For Kenics static mixers[35] a rule of thumb is:

$$\text{Percent of compressed air which dissolves} = (\text{depth in feet}) - 2.5 \qquad (39)$$

The deeper the tank, the higher is the pressure required from the compressor. The work done by the compressor at low pressures when the compressibility factor equals one is given by[36]:

$$HP = 0.00078 \frac{WT}{Mne} \left[\left(\frac{P_2}{P_1} \right)^n - 1 \right] \qquad (40)$$

where W = massflow, lb/hr

T = inlet temperature, °R

M = molecular weight = 28.8 for air

n = approx. 0.286 for air in adiabatic compression
approx. 0.408 for air in polytropic compression

e = efficiency = 0.7

P_1, P_2 = inlet and outlet absolute pressures.

Adiabatic compression is probable and the horsepower is very close whether adiabatic or polytropic compression is assumed. (Reference 28 gives the formula for adiabatic compression.) If the inlet temperature is taken to be 80°F = 540°R (which is necessary for design, but high for a year-round average), then for air:

$$HP = 0.073\ W \left[\left(\frac{P_2}{P_1} \right)^{0.286} - 1 \right] \qquad (41)$$

Equations (39) and (41) were used to determine the theoretical horsepower to dissolve 1,000 lb O_2/hr at various depths. The pressure was taken to be (1.2 x depth). Air contains 23 wt% oxygen. The results are:

Depth (ft)	Fraction of Air Which Dissolves	Air to be Compressed (lb/hr)	Pressure Drop (psi)	Compressor hp
10	0.075	57,800	5.2	382
20	0.175	24,800	10.4	300
30	0.275	15,700	15.6	264
40	0.375	11,600	20.9	244

These are calculated power requirements without allowance for inefficiencies. The real power requirements for surface aerators probably would fall in the range 400-500 hp. The capital cost of compressors is very dependent on the pressure ratio because the design changes if a higher pressure outlet is required. Diffusion systems will tend to cost more than surface aerators to install but less to run. Diffusion systems should be considered in most situations.

5.3.4 Examples

A definitive study has not been made of aeration in the two examples under consideration. The cost of excavation enters into the economics and was not known. Surface aerators have been discussed with only one manufacturer, Bird Machinery, South Walpole, Mass., and the following is a possibility, not a recommendation.

Example 1. The horsepower for surface aeration is

$$\frac{2{,}500 \text{ lb BOD}}{10^6 \text{ lb water}} \times (0.3 \times 8.33 \times 10^6)\ \frac{\text{lb water}}{\text{day}} \times \frac{1}{43}\ \frac{(\text{hp})(\text{day})}{\text{lb BOD}} = 145 \text{ hp}$$

Two 75 hp aerators can be used. The aeration basin which has 107,000 ft^3 liquid capacity can be 20 ft deep x 52 ft wide x 103 ft long. This is quite deep and draft tubes will be needed to ensure mixing near the bottom. Some advantage of partial plug flow can be taken by having the inflow and outflow on the short sides.

Example 2. The horsepower for surface aeration is:

$$\frac{18{,}000 \text{ lb BOD}}{10^6 \text{ lb water}} \times (0.17 \times 8.33 \times 10^6)\ \frac{\text{lb water}}{\text{day}} \times \frac{1}{43}\ \frac{(\text{hp})(\text{day})}{\text{lb BOD}} = 593 \text{ hp}$$

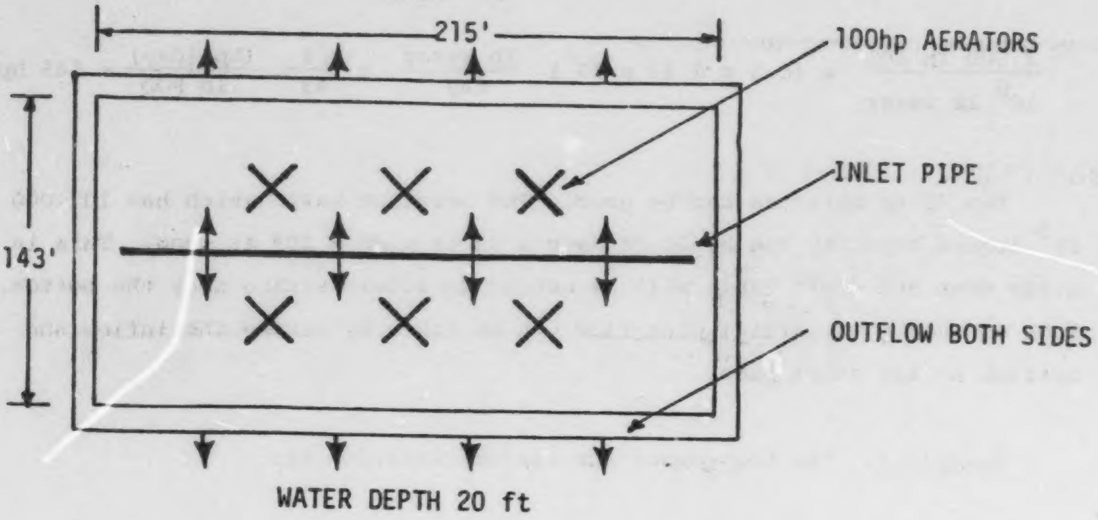
Good mixing is required. Six 100 hp aerators can be installed in a basin 20 ft deep x 143 ft wide x 215 ft long. Inflow and outflow should be on the long side. Possible arrangements for both basins are shown in Figure 5-9.

In both examples deep basins have been chosen to suit the particular aerators under consideration; other possibilities should be sought.

5.4 Operation

Of all the treatments likely to be used for treating wastewater from coal conversion, biological treatment appears to have the least firm experimental basis for design. Therefore, a summary of operating techniques follows with some emphasis on how to obtain better information for future designs.

STEP 1.


215'
100hp AERATORS
INLET PIPE
143'
OUTFLOW BOTH SIDES
WATER DEPTH 20 ft

STEP 2.

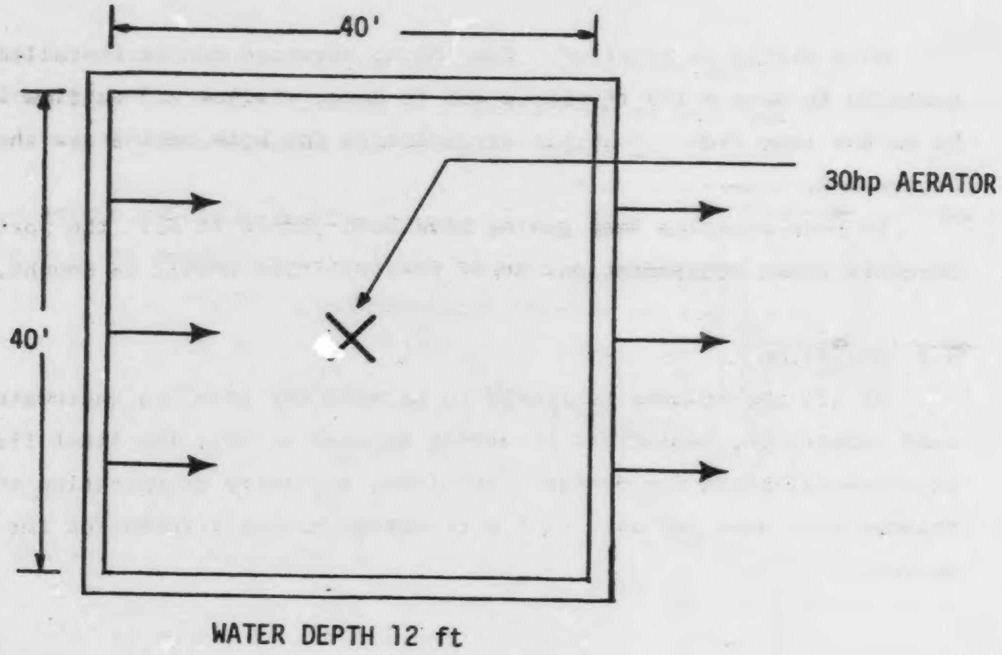

40'
30hp AERATOR
40'
WATER DEPTH 12 ft

Figure 5-9. Aeration basins for air activated sludge, Example 2.

5.4.1 Variables Under the Operator's Control

Activated sludge processes are affected by many process variables. Once the plant is built, some of these are fixed. Fixed parameters include the aeration basin volume, the aerators, the clarifier size, and the wastewater flow and concentration. Parameters over which the operator has some control are shown in Table 5-9.

Parameter 1: Oxygen Utilization Rate (OUR)

Because oxygen usage is directly related to the removal of biodegradable organics, the OUR in the aeration basin serves as a measure of the biochemical activity in the system. The value of OUR will generally range from 10 to 70 mg/l/hr. Excessively low OUR indicates low biochemical activity, which may be due to non-biodegradability of the pollutant or lack of active biota in the aeration basins. Too high an OUR, on the other hand, might lead to too low a level of dissolved oxygen in the mixed liquor, and oxygen transfer may be limited. The amount of biological solids may be controlled by adjusting the return sludge flow rate, and OUR may thus be controlled to a certain extent. The dissolved oxygen concentration in the mixed liquor should be maintained at no less than 2 mg/l.

In a high purity oxygen activated sludge system we must determine the coefficients related to gas transfer. These include the Henry constants, H_i, and the overall gas transfer coefficient, K_La, as shown in Section 5.5. The values of H_i for various gas constituents in pure water can be found from standard references, but the value of K_La will have to be determined in the actual operation because it is highly dependent on the actual design and operation.

Under a steady state condition, the Equations of Table 5-15 may be rearranged to yield:

$$K_La = \frac{a' \dfrac{kX\,C_{4n}}{K_s + C_{4n}} - b'X - \dfrac{Q_1}{V_n}\left(C_{1,n-1} - C_{1,n}\right)}{\left(H_1 P_{1,n} - C_{1,n}\right)}$$

In the actual operation of a demonstration plant, all terms on the righthand side of this Equation may be determined and the K_La can be calculated.

TABLE 5-9 ACTIVATED SLUDGE PROCESS CONTROL PARAMETERS

Parameter	Variability	Control	Comment
1. Oxygen Utilization Rate (mg/l/hr)	Some	Some	Control may be accomplished by adjusting return sludge flow rate.
2. Sludge Wasting	Some	Yes	Control is based on the value of sludge residence time which depends on the BOD removal and solids separation to be achieved in final clarifiers.
3. Return Sludge Flow Rate	Within design range	Yes	Hourly adjustment to be considered on the basis of sludge settling characteristics and final clarifier depth of sludge blanket.
4. Depth to Clarifier Sludge Blanket	7 - 10 ft	Yes	Control through adjustment of return sludge flow rate and sludge wasting.
5. Sludge Settling Characteristics	Some (SVI) = 50 to 100)	Some	Control through adjustment of sludge wasting.

To determine the actual oxygen requirement in terms of pounds of oxygen required per pound of BOD removed, the COD balance technique discussed in Section 3 is also applicable to the High Purity Oxygen Activated Sludge System.

Parameter 2: Sludge Wasting

Sludge wasting is one of the most important parameters over which the operator has complete control. Its control is based on the value of θ_c, which has been defined by Equations (5), (6) and (7). Equation (7) is

$$\theta_c = \frac{VX}{wX_r}$$

From this Equation the sludge wasting rate, w, can be calculated when the values of V, X, X_r and θ_c are known. V is fixed by design. X and X_r have to be actually measured by the operator. The value of θ_c usually ranges between 3 and 40 days, although a single θ_c value is used for design calculations. This design θ_c value serves as a guideline for startup and after several months of operation, the operator will be able to determine what the optimum θ_c range should be to produce an effluent of the desired quality. The operator should also try to waste sludge as uniformly as possible, that is, to avoid wasting in surges so that the potential for unstable conditions may be minimized.

Parameter 3: Return Sludge Flow Rate

The purpose of returning sludge from the clarifier to the aeration basin is to sustain a desirable MLSS level to react with the biodegradable organics. If the return sludge flow rate, represented by q in the design equations, is too low, the following undesirable conditions may develop:

- There may be insufficient MLSS to effectively react with the incoming BOD in the aeration basin, causing a deterioration in effluent quality.
- The larger accumulation of sludge in the clarifier may create a thicker sludge blanket at the clarifier bottom, which may allow more solids to escape in the overflow.

The relationship between MLSS, i.e. X, and q or r (recycle ratio) was previously derived through a mass balance in Equation (16):

$$X = X_r\left(\frac{q + w}{Q + q + w}\right) = X_r\left(\frac{r + \frac{w}{Q}}{1 + r + \frac{w}{Q}}\right)$$

With constant X_r and $\frac{w}{Q}$, Equation (16) shows that as r increases, X will also increase, although not proportionally.

Too high a return sludge rate should also be avoided for the following reasons:

- As r increases, there will be less sludge consolidation in the clarifier, and therefore X_r will decrease in Equation (16).
- As X increases, the sludge settling velocity, V, will decrease in accordance with Equation (29):

$$V_i = aX_i^{-n}$$

Eventually there will be a limiting solids flux, preventing any further increase of solids transport from clarifier to aeration basin by increasing the recycle ratio r. Qualitatively this has been shown in Figure 5-5, which can be quantitatively determined by the operator.

Although the purpose of adjusting the return sludge rate is to shift the biological solids from the clarifier to the aeration basin or vice versa, limits must be observed at both high and low ends. The recycle ratio r generally ranges from 15 to 100%.

Parameter 4: Depth to Sludge Blanket in the Clarifier

The depth of sludge blanket provides the operator with an indication of the sludge settling characteristics and the need for adjusting return sludge rate and/or sludge wasting.

This parameter is determined by measuring the depth from the water surface to the top of the sludge blanket using a sludge blanket depth finder or equivalent devices and measurement should be done at least once every eight-hour shift and can be made by inserting a transparent tube, closing the top end, lifting out the full tube and measuring it.

Parameter 5: Sludge Settling Characteristics

Sludge volume index (SVI) may be used as a measure of the sludge settling characteristics. This involves the standard settling test which is usually conducted with the aeration basin mixed liquor in a one-liter graduated cylinder. After 30 minutes of settling, the volume of sludge is measured, and SVI in ml per gram can be calculated as follows:

$$\text{SVI}(\text{ml/gm}) = \frac{\text{Volume of sludge}(\text{ml/l})}{\text{MLSS}(\text{mg/l})} \times 1{,}000$$

Sources for the required tests are given in Table 5-8.

In general, sludges with an SVI between 50 and 100 have good settling characteristics. As SVI increases, the settleability becomes poorer. Common control measures include adjusting Θ_c and/or chemical treatments, such as the addition of flocculating agents.

5.4.2 Startup

Before the actual startup, all structural, mechanical and electrical components should be carefully checked, especially the following items:

- The drive mechanisms of the mechanical aerators and clarifier scrapers and skimmers
- All pumps
- All gates and valves
- All effluent weirs in the aeration basins and final clarifiers should be level.

The following sequence of steps should be followed to start:

(1) Fill the aeration basins with the bacteria seed and river water. (Sources of bacteria will be discussed later.)

(2) Turn on all mechanical aerators.

(3) Slowly start the inflow of wastewater into the aeration basins, and the aeration basin effluent will start to fill the clarifier. The purpose is to build up sludge. The quickest measurement is the oxygen uptake rate and we want to obtain a steady increase in OUR. Let in wastewater at such a rate that OUR increases. We also want a steady increase in MLVSS, but this takes longer to determine. If the increase is not found, the first possibility is that the sludge is not acclimatized, that is, the waste is toxic. In this event slow down the feed. The effluent quality is not controlled during start-up and if it is unsatisfactory, the effluent must be returned to the equalization pond.

(4) When the clarifier is about 3/4 full, start the sludge collection mechanisms and the recycle sludge pumps. Set the pumps at 100% recycle to return all settled solids in the final clarifier to the aeration basins to build up the activated sludge concentration, X.

(5) Steps (1) through (4) may be applied to Stage 2 of the activated sludge process except that the inflow of wastewater in Step (3) will be replaced by the overflow from the Stage 1 clarifier.

(6) At intervals, probably every four hours, check the dissolved oxygen (DO) level in the aeration basins to ensure a minimum of 2 mg/l.

The activated sludge will take several weeks to develop in the aeration basins. Sludge recycle rate should be gradually reduced as the mixed liquor volatile suspended solids, X, increases. Sludge wasting should be started when X exceeds 4,000 mg/l. Adjustments of return sludge rate, q, and sludge wasting rate, w, will have to be made to maintain a steady state.

5.4.3 Operation and Control

The activated sludge process is designed to be run continuously and semi-automatically. The equalization basin effluent will be uniformly fed to the aeration basins and mixed with the returned sludge. After contact in the aeration basin, the mixed liquor then flows by gravity to the clarifier. The clarified effluent overflows to any downstream processes, and the settled downflow will be pumped to a sludge holding tank. Part of the sludge will be wasted from the holding tank to maintain θ_c and the remainder will be pumped back to the aeration basins to react with the wastewater influent.

The process controls that the operator can regulate are sludge return rate, q, and sludge wasting rate, w. The relationships between the controls and expected responses of the activated sludge process are detailed in Table 5-10. Based on an understanding of these relationships, a list of suggested actions to cope with various conditions of process parameters is given in Table 5-11. The same principles apply to the operation and control of both stages of the activated sludge process.

5.4.4 Nutrients and Activated Sludge Seed

Phosphorus has been considered the only mineral nutrient supplement required for the activated sludge. However, a number of studies have advocated the addition of other mineral nutrients. In a study of the applicability of coke plant water treatment technology to coal gasification, Parsons and Nolde[20] based the mineral requirements on the elemental composition of typical dry bacterial protoplasm, which is shown in Table 5-12. A comparison between the approximate quantities of nutrients present in Synthane coal gasification condensate and coke plant ammonia still feed, and the bacterial composition from Table 5-12 is made in Table 13. The comparison shows that Synthane condensate is more deficient in phosphorous, potasium, iron and magnesium than the ammonia still feed. However, this does not represent a universal conclusion because the condensate composition depends on the type of coal feed and the upstream treatment processes.

In a recent bench-scale pilot study of the biotreatment of a weak ammonia liquor from a coke plant which had been pretreated by multi-stage flash evaporation[21], Adams supplemented various mineral nutrients to the raw wastes in the ratios shown in Table 5-14. The ratios are based on a literature review of the nutrients required for activated sludge and the relative amounts of minerals that are added are related to the BOD of the wastewater. In their experimental study they found that filamentous sludges were produced in the absence of the nutrients shown in Table 5-14.

TABLE 5-10 RELATIONSHIP BETWEEN PROCESS CONTROLS AND EXPECTED RESPONSES OF ACTIVATED SLUDGE PROCESS

	Process Control Parameters		Expected Process Responses		
Case	Return Sludge Flow Rate, q	Sludge Wasting Rate, W	Sludge Settling Characteristics	Solids Mass Wasted, P_x	Solids Retention Time, θ_c
1.	Increase	Constant	1) Sludge Volume Increases 2) X_r Decreases	Less	Increases
2.	Decrease	Constant	1) Sludge Volume Decreases 2) X_r Increases	More	Decreases
3.	Constant	Increases	No Effect Initially, then Follows Case 2	More	Decreases
4.	Constant	Decreases	No Effect Initially then Follows Case 1	Less	Increases

TABLE 5-11 SUGGESTED ACTIONS FOR VARIOUS CONDITIONS OF PROCESS PARAMETERS

Process Parameter	Condition	Suggested Action
Dissolved Oxygen (DO) in Aeration Basins	(1) Satisfactory (2.0-4.0 mg/l)	NONE
	(2) Too high (>4.0 mg/l)	Reduce aerator speed from high to low
	(3) Too low (<2.0 mg/l)	(1) Increase aerator speed from low to high (2) Measure oxygen uptake rate (OUR) on other sections of the basin to determine if primary effluent feed to all sections should be modified
Mixed Liquor Volatile Suspended Solids (MLVSS)	(1) Satisfactory (3,000-4,000 mg/l)	NONE
	(2) Too high (>4,000 mg/l)	Increase sludge wasting slowly
	(3) Too low (<3,000 mg/l)	Decrease sludge wasting slowly
Depth to Sludge Blanket	(1) Satisfactory (7-10 ft)	NONE
	(2) Too large (> 10 ft)	Increase Return Sludge Rate or decrease Sludge Wasting Rate
	(3) Too small (< 7 ft)	Increase Sludge Wasting Rate or decrease Return Sludge Rate

TABLE 5-12 REPRESENTATIVE ELEMENTAL COMPOSITION OF DRY BACTERIAL PROTOPLASM (From Reference 20)

	Wt. %		Wt. %
C	50	Na	0.7
H	5.8	K	0.5
O	27	Ca	0.7
N	12	Mg	0.5
P	2.5	Fe	0.1
S	0.7		

TABLE 5-13 HYPOTHETICAL COMPARISON OF TRACE NUTRIENT COMPOSITION VS. INDICATED BACTERIAL REQUIREMENT FOR SYNTHANE CONDENSATE AND COKE PLANT AMMONIA STILL FEED (From Reference 20)

	Indicated Requirement lb/1,000 tons	Synthane Condensate Indicated Present lb/1,000 tons	Coke Plant Ammonia Still Feed Indicated Present lb/1,000 tons
Ca	10	5.1	5.9
Fe	2.8	0.28	3.2
K	14	0.78	16
Mg	14	1.6	3.5
Na	20	19	95
P	70	0.12	57

TABLE 5-14 REQUIRED NUTRIENTS FOR ACTIVATED SLUDGE (From Reference 21)

	gm/30 1	mg/1
Manganous Sulfate	0.831	27.7
Manganous Sulfate: H_2O	0.930	31.0
Cupric Chloride	0.969	32.3
Sub. Copper Sulfate: $5H_2O$	1.670	55.6
Zinc Sulfate	1.20	40.0
$ZnSO_4:7H_2O$	2.14	71.3
Molybdic Anhydride	1.93	64.3
Sub. Ammonium Molybdate		
Selenium Oxide	$6(10^{-6})$	$.2(10^{-3})$
Magnesium Sulfate	45.15	1,505.0
Magnesium Sulfate: $7H_2O$	92.4	3,080.0
Sub. Magnesium Chloride		
Cobalt Chloride	1.1	36.6
Cobalt Chloride: $6H_2O$	2.01	67.0
Calcium Chloride	51.2	1,706.6
Sodium Carbonate	14.46	482.0
Sub. Sodium Bicarbonate	28.92	964.0
Sodium Chloride	0.395	13.1
Sub. Sodium Sulfate		
Potassium Chloride	25.9	863.3
Ferric Chloride	107.0	3,566.6
Ferric Chloride: $6H_2O$	178.0	5,933.3

Amount/Day (liters) = BOD in mg/1 x 10^{-5} x Flow in 1/Day

The addition of nutrients in the ratios shown in Table 5-12 reduced the SVI from 250 - 350 to 100 - 200 range.

Although the above data will serve as a general guideline, the exact quantities of mineral nutrients required will have to be determined on a case-by-case basis.

The mineral nutrient requirements of activated sludge should be first studied by laboratory experimental procedures involving several culture transfers in the determination of BOD rates[22]. The results of these experiments should then be tested on a continuous-flow basis with particular emphasis on the settleability of the generated sludge as measured by SVI.

The activated sludge seed used to start up the plant should be obtained from a source which is free from pathogenic organisms. This is because the treated water may be used as cooling tower makeup and every precaution should be taken to prevent or minimize the potential spread of any harmful organisms in cooling tower drift or blowdown. Potential sources for the activated sludge seed include commerical biological cultures such as mutated Pseudomonas sp., or the activated sludge successfully treating a similar industrial wastewater such as coke plant wastes, in which no contamination by pathogens has occurred.

5.4.5 Determination of Improved Process Constants

Published process constants on related waters vary over a wide range. This uncertainty makes it necessary for the constants to be determined in laboratories and demonstration plants so that any future plants can be designed better. Detail on laboratory determinations will be found in Reference 45. Demonstration plants should be designed with flexibility, and the determinations of process constants should be made.

A. Biokinetic Constants, k, K_s, Y, k_d

These four biokinetic constants are evaluated graphically as shown on Figures 5-2 and 5-3, which are graphs of Equations (3) and (2). All values plotted should be taken under steady state corresponding to specific values of θ_c as calculated by Equation (6). The general procedures are:

1) After startup select an appropriate value of X, say 3,000 mg/l, and adjust the sludge wasting rate so that a steady state can be maintained.

2) Measure S_o, S_1, Q, w, X, X_r, X_e.

3) Calculate $\frac{1}{X}\frac{dS}{dt} = \frac{Q(S_o - S_1)}{XV}$

$$\frac{1}{X}\frac{dX}{dt} = \frac{wX_r}{VX} = \frac{P_x}{XV}$$

$$\theta_c = \frac{VX}{wX_r + QX_e}$$

4) Increase X by reducing w gradually.

5) Repeat steps 2), 3) and 4) until at least five sets of data are obtained.

6) Plot $\frac{1}{X}\frac{dS}{dt}$ vs. S as in Figure 5-2 and evaluate k and K_s.

7) Plot $\frac{1}{X}\frac{dX}{dt}$ vs. $\frac{1}{X}\frac{dS}{dt}$ as in Figure 5-3 and evaluate Y and k_d.

It is also desirable to find the maximum X which can be maintained for satisfactory operation, i.e., without exhausting dissolved oxygen in the mixed liquor with aerators operating at full capacity, and without excessive deterioration of effluent quality.

The F/M ratios, if desired, may be calculated from θ_c by using Equation (12). The substrate S may represent any of the following parameters: phenols, BOD, COD or TOC. It is recommended that all of these parameters be measured when any S is to be determined.

The effects of trace nutrients, if any, may be evaluated by comparing values of biokinetic constants with nutrients added and those without.

B. Oxygen Requirements

The oxygen requirements may be determined by OUR measurements or total COD balance as explained. Because of the high BOD strength of coal conversion wastewaters, total COD balance would probably give the most accurate results. The OUR measurements are fast and simple, and may serve to quickly identify any potential trouble in the bioreactor. For instance, a low OUR indicates slow bio-oxidation which may be due to the presence of toxic substances in the feed.

The oxygen requirements determined in accordance with the procedures given are usually in pounds of O_2 required per day. To present such data in a more meaningful way, the total oxygen requirements may be divided into two major components as in the following equation:

$$\text{lb } O_2/\text{day} = a' (\text{lb BOD}_5 \text{ removed/day}) + b' (\text{lb MLVSS})$$

The coefficient, a', represents the oxidation of BOD_5 in the wastewater. The coefficient, b', represents the endogenous respiration rate. The amount of BOD_5 removed per day may be calculated from Equation (18), and the amount of MLVSS is equal to VX.

The total oxygen requirements will be a function of the BOD/COD ratio. If the wastewater feed varies in BOD/COD, extra care must be taken to ensure that total oxygen requirements are determined under steady state conditions when the BOD/COD ratio is constant.

C. Solids Settling Experiments

The settling characteristics of activated sludge have been discussed and the relationship between the settling velocity, V_i, of the solids at concentration, X_i, has been described by Equation (29):

$$V_i = a X_i^{-n}$$

One objective of solids settling experiments is to evaluate coefficients a and n from multiple batch settling tests as described below:

1) The mixed liquor from the sludge holding basin is diluted with treated water to obtain various solids concentrations within the range of concentrations expected to be maintained in the aeration basin.

2) Pour the mixed liquors into standard one-liter graduate cylinders, each with a different solids concentration, X_i. Each test cylinder should be equipped with a variable-speed stirrer.

3) Mix the solids gently in each cylinder to obtain homogeneity, then stop mixing and allow solids to settle under quiescent conditions.

4) A solids-liquor interface will form and its position vs. settling time is recorded.

5) Plot the position of interface vs. settling time as shown in Figure 5-10.

6) The slope of the straight line portion of the settling curve in Figure 5-10 is the settling velocity, V_i, of the sludge at an initial solids concentration of X_i. This settling velocity is also referred to as zone settling velocity (ZSV).

7) Plot V_i vs. X_i on a log-log graph paper as shown in Figure 5-4 and evaluate a and n from the straight line obtained.

8) At the completion of settling tests, siphon off the clear supernatant and determine the solids concentration in the remaining sludge blanket, which may be a good measure of X_r in the full scale clarifier.

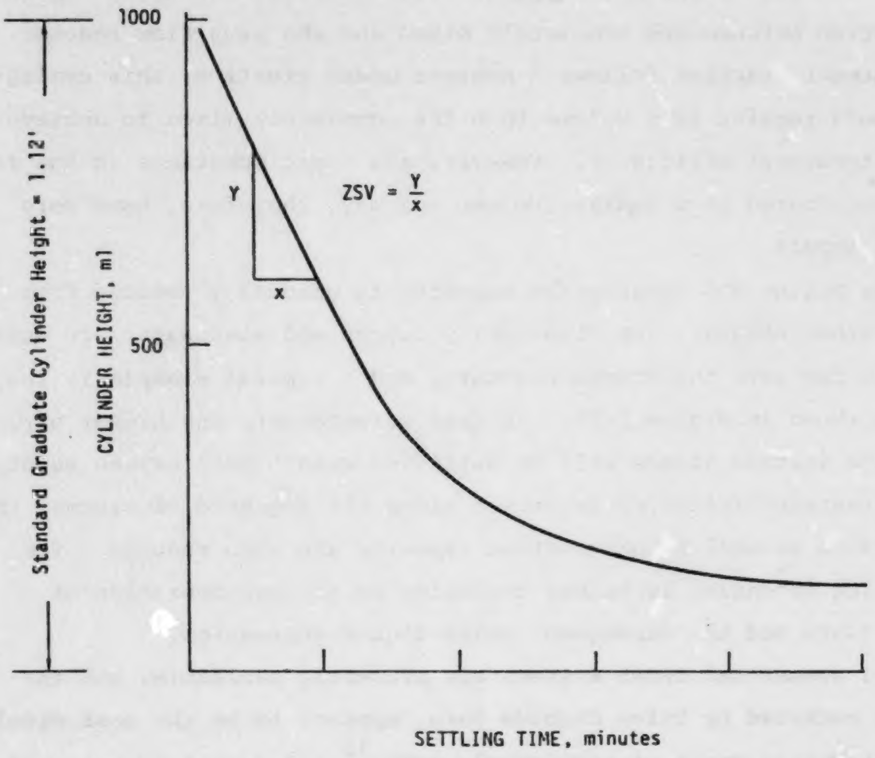


Figure 5-10. Sludge settling curve.

5.5 High Purity Oxygen Activated Sludge (HPOAS) Process

HOPAS represents a modification of AAS with major changes in the following:

1. High purity oxygen is used in place of ordinary air to supply the oxygen needed to oxidize the organics. Because of the higher partial pressure of oxygen in the gas phase, the dissolved oxygen can be maintained at a higher concentration in HPOAS than in AAS system.

2. Staged covered reactors are used to facilitate the transfer of oxygen from the gas to the liquid phase. The reactors in stages represent a configuration between the completely mixed and the plug flow reactor. If the treatment reaction follows a nonzero order kinetics, this configuration should require less volume than the completely mixed to achieve equivalent treatment efficiency. However, any toxic substance in the feed would be distributed in a smaller volume and may, therefore, have more detrimental impact.

3. The mixing and oxygenation capacity is gradually reduced from the initial to final stages. The high-purity oxygen and wastewater are usually concurrently fed into the staged reactors, and a typical example is the UNOX system shown in Figure 5-11. In this arrangement, the higher oxygen demand in the initial stages will be satisfied with higher oxygen supply. As the biotreatment intensity decreases along the sequence of stages, the required mixing as well as oxygenation capacity are also reduced. The reduced mixing intensity is highly conducive to the agglomeration of biological flocs and the subsequent solid-liquid separation.

Several commercial HPOAS systems are presently available, and the UNOX system marketed by Union Carbide Corp. appears to be the most widely used for the biotreatment of industrial wastes[11]. A recent overview of the UNOX process can be found elsewhere[12,30].

5.5.1 The Biokinetic Model. In general, it has been observed[13,14] that HPOAS seems to be more efficient than AAS in removing BOD under higher organic loadings, and also tends to produce less biomass for sludge disposal. These advantages of HPOAS are not to be attributed to any metabolic changes in the microorganisms indigenous to the activated sludge process. Biochemical analysis of sludge samples from both AAS and HPOAS systems showed no difference in all constituents[15] in terms of their percentages of volatile suspended solids.

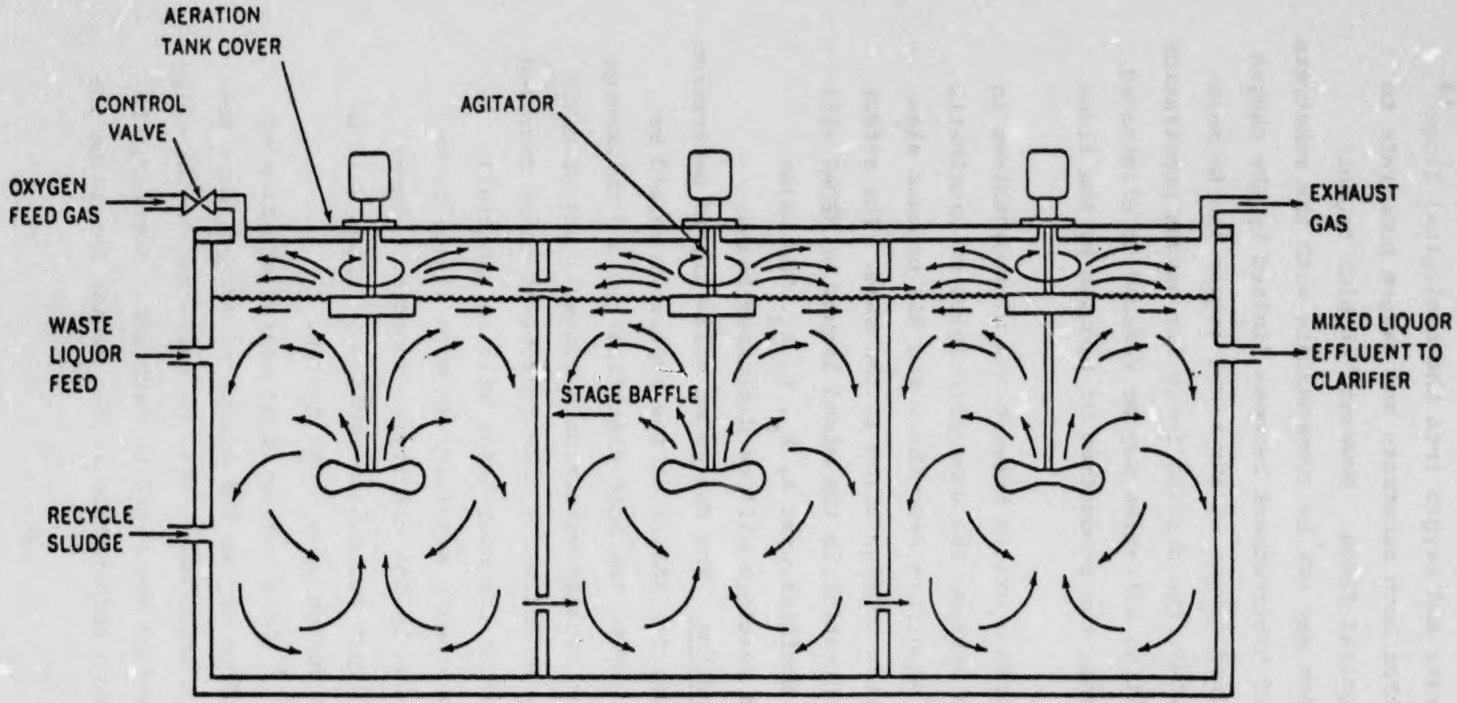

AERATION TANK COVER
CONTROL VALVE
OXYGEN FEED GAS
AGITATOR
EXHAUST GAS
WASTE LIQUOR FEED
STAGE BAFFLE
MIXED LIQUOR EFFLUENT TO CLARIFIER
RECYCLE SLUDGE

Figure 5- 11. Schematic diagram of UNOX system with surface aerator (3 stages shown).

A widely accepted hypothesis accounts for the difference as different rates of penetration of substrate and oxygen into the biological flocs[13]. The ideal situation would be that both substrate and oxygen penetrate to an equivalent level into biological flocs. However, at high organic loadings, the oxygen penetration may not be commensurate with the substrate penetration and the kinetics of biotreatment becomes limited by the oxygen penetration. Since the dissolved oxygen of the mixed liquor can be maintained at a higher level in HPOAS, the driving force for oxygen penetration is larger, and the oxygen-limiting situation may be reduced or eliminated. Under a more aerobic environment, the production of biomass by the flocs will be less.

Since no biological difference exists between the microorganisms in the AAS and those in the HPOAS system, the same principles of biokinetic modeling may be applied. The equations describing the AAS process also describe the HPOAS if the reactor configuration is the same. The effect of high dissolved oxygen concentration in the mixed liquor of HPOAS will be reflected in the values of coefficients: k, K_s, Y, k_d. The major effects of using staged closed reactors will be discussed below.

5.5.2 Solid-Liquid Separation. The design of solid-liquid separation for HPOAS is identical with that for AAS, i.e. the separator should be designed to satisfy the requirements for both clarification and thickening. However, since the HPOAS system usually maintains a higher level of MLVSS in the bioreactor, the ability to deliver a high concentration of recycled sludge from the solid separator to the bioreactor will be especially important i.e. the design of the solid separator is more likely to be controlled by the thickening than by the clarifying function. Those equations and discussions developed for solid-liquid separation will be particularly important for the design of a HPOAS system.

It is commonly accepted[12,13] that the settling characteristics of activated sludge improve significantly as the dissolved oxygen increases from 2 to 5 mg/l or more. This improvement will be reflected in the value of the coefficients a and n used in the settling equation. However, the general procedures for using such information in the design should be the same as that described.

5.5.3 Oxygen Transfer. The principles and discussions already given are generally applicable to HPOAS except for certain additional complications primarily due to the reactor configuration used. The use of staged closed reactors for HPOAS introduces the following conditions different from those for AAS:

1. While the closed reactor is desirable in maintaining relatively higher partial pressure of oxygen in the gas space inside each reactor, it also tends to collect any gases which may be stripped out of the liquid phase as a result of the mixing action. These gases include nitrogen (N_2), carbon dioxide (CO_2) and any volatile organics originally present in the wastewater. The N_2 content in the wastewater is due to its solubility, but the CO_2 will be mostly from biochemical oxidation.

2. The compositions of both gas and liquid phases will change from stage to stage in a system depicted in Figure 5-11. Since the oxygen is fed co-currently with the wastewater, the partial pressure of oxygen will be reduced from stage to stage because of the oxygen demand of wastewater and the diluting effect of the stripped gases.

Although the overall objective of oxygen transfer remains the matching of oxygen supply and demand, this task becomes complicated as the objective should be achieved in each stage under dynamic conditions. Obviously the rational approach would be to develop a mathematical model describing the mass transfer of key constituents in both gas and liquid phases so that the condition of each stage can be readily computed. This modeling approach will be further developed.

The collection of any volatile organics in the gas phase may facilitate the treatment of gaseous emissions from an HPOAS plant should it become necessary. This should be considered as an advantage of the HPOAS system.

5.5.4 Cooling of Mixed Liquor. One of the complications introduced by enclosing the reactors is the rise of water temperature due to the oxidation of biodegradable organics. Assuming 100% biodegradability, the oxidation of phenol can lead to about 1°F temperature rise per 165 mg/l BOD removed.

Biological agents are known to be temperature sensitive. Mesophilic bacteria, which constitute the bulk of activated sludge, do not operate effectively of the temperature rises beyond about 104°F (40°C). In the aerobic biological treatment of coke plant wastes, it has been recommended[16] that the water temperature be 95-100°F throughout the year. When a high level of BOD removal is to be achieved by HPOAS, the rise in water temperature may become excessive and a means of cooling becomes necessary. One possibility is to control the temperature by internally recycling the wastewater stream (mixed liquor) from the last stage, back to the first stage. This has the possible additional advantage of diluting potentially toxic materials in the concentrated wastewater.

5.5.5 A Model for HPOAS. As mentioned, a rational approach to matching the oxygen supply with demand may be to develop a mathematical model to account for the material balance of key constituents in both gas and liquid phases of each stage of the reactors. Such a model has been developed by Mueller et al for a municipal wastewater plant and successfully used to predict changes in operation[17]. In this section basic equations will be developed and the general approach for coal conversion wastewaters using the kinetic equations developed for AAS will be described.

The key constituents in the liquid phase are dissolved oxygen (O_2), carbon dioxide (CO_2), nitgrogen (N_2), BOD and pH. In the gas phase the parameters of concern are the partial pressures of O_2, CO_2, N_2. In addition, since a net gas transfer occurs from the gas to liquid phase, the gas flow rate is also of concern. Thus there are, in total, nine key parameters which are interrelated and whose magnitudes are to be determined for every stage of reactor[17,18].

The principle of mass conservation will be applied to a reactor configuration shown in Figure 5-12. Wastewater and oxygen are cocurrently applied to a series of n stages of bioreactors, and the outflow of liquid and gas from the (n-1)th stage is the inflow to the n'th stage. The liquid and gas phases of each stage are assumed to be completely mixed. The concentration of the i'th liquid constituent in the n'th stage is denoted by $C_{i,n}$, and the partial pressure of the i'th gas constituent in the n'th stage by $P_{i,n}$.

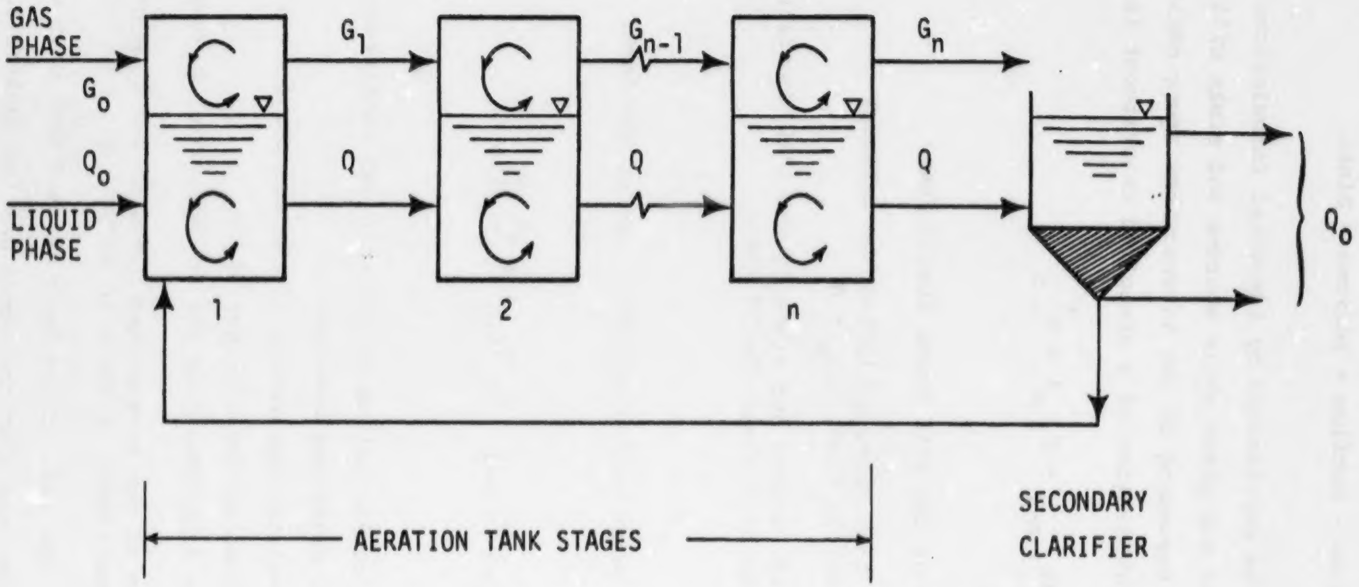

GAS
PHASE
G_o
Q_o
LIQUID
PHASE
G_1
Q
G_{n-1}
Q
G_n
Q
1
2
n
Q_o
AERATION TANK STAGES
SECONDARY
CLARIFIER

Figure 5-12: Schematic diagram of staged bioreactors for HPOAS
(From Reference 17)

The general mass conservation equation is:

$$\text{Change} = \text{Inflow} - \text{Outflow} + \text{Sources} - \text{Sinks} \qquad (42)$$

The inflow and outflow may be represented by identical formulations for any constituent in the liquid or gas phase while sources and sinks will vary from constituent to constituent depending on the interactions among constituents. In the liquid phase the concentration of a dissolved constituent is governed by:

$$\frac{dC_{i,n}}{dt} = \frac{Q}{V_n^l} (C_{i,n-1} - C_{i,n}) + S_{i,n}^l \qquad (43)$$

where

V_n^l = volume of the n'th stage liquid phase

Q = liquid flow rate, including the influent plus recycle flows = $Q_o + q$

$S_{i,n}^l$ = sum of sources and sinks of the i'th constituents in the n'th stage liquid phase

t = time

In the gas phase the mass conservation equations are of the form:

$$\frac{M_i V_n^g}{RT} \frac{dP_{i,n}}{dt} = \frac{M_i}{RT} (G_{n-1} P_{i,n-1} - G_n P_{i,n}) + V_n^l S_{i,n}^g \qquad (44)$$

where

M_i = molecular weight of the i'th gas constituent

R = universal gas constant

T = absolute temperature of the gas phase

V_n^g = volume of the n'th gas stage

G_{n-1} = gas flow rate from the (n-1)th to n'th stage

$S_{i,n}^g$ = sum of the sources and sinks of the i'th gas constituent in the n'th stage.

In writing Equations (43) and (44) it has been assumed that each volume, V_n^l and V_n^g, is constant in time, and that the ideal gas law applies for each gas constituent.

The interactions among these constituents, which constitute various sources and sinks, are described in the following paragraphs:

1. Gas transfer between gas and liquid phases.

As oxygen is introduced into a bioreactor, three transfer mechanisms occur: (1) O_2 is transferred from the gas to liquid phase; (2) N_2 originally present in the liquid is initially transferred to the gas phase; and (3) CO_2 produced by the biochemical reaction is transferred from the liquid to gas phase.

The rate of gas transfer across the gas-liquid interface is proportional to both the driving force (the difference between the dissolved gas saturation and the actual concentration) and the overall gas transfer coefficient, $K_L a$. For a dissolved gas in water, its transfer rate can be expressed as:

$$\frac{dC_i}{dt} = K_L a\ (C_{s,i} - C_i) \tag{45}$$

where

C_i = actual concentration of the dissolved gas, i

$C_{s,i}$ = saturation concentration of the dissolved gas, i, which can be related to its partial pressure in the gas phase by Henry's Law

$$C_{s,i} = H_i P_i \tag{46}$$

where

H_i = Henry's constant for gas i.

2. Consumption due to biochemical oxidation.

Biochemical oxidation leads to a consumption of O_2 and BOD. The total oxygen requirements may be expressed as:

$$\text{lb } O_2\text{/day} = a'(\text{lb BOD}_5 \text{ removed/day}) + b'(\text{lb MLVSS}) \tag{47}$$

The coefficients a' and b' will be used to formulate the sinks for O_2 in the liquid phase. The consumption of BOD has been described in the form:

$$\frac{dS}{dt} = \frac{KXS}{K_s + S} \qquad (48)$$

The terms in Equation (48) have been defined in the section on air activated sludge.

3. Production due to biochemical oxidation.

While O_2 is consumed during biochemical oxidation, CO_2 is produced. The moles of CO_2 produced per mole O_2 consumed is called the respiratory quotient (RQ) and its value may vary with loading conditions and can be experimentally determined. The production of CO_2 may be expressed in the same fashion as Equation (47):

$$\text{lb } CO_2\text{/day} = a''(\text{lb } BOD_5 \text{ removed/day}) + b''(\text{lb MLVSS}) \qquad (49)$$

where

$$\frac{a''}{a'} = \frac{b''}{b'} = RQ\left(\frac{44}{32}\right) \qquad (50)$$

The various sources and sinks for key constituents in the liquid and gas phases are summarized in Table 5-15.

As shown in Table 5-15, the only interaction with N_2 in the liquid phase is the interphase gas transfer; no other reaction is assumed to take place. Also no BOD transfer from the liquid to gas phase has been assumed. Because no reaction occurs in the gas phase, the only source of each species is that through interphase gas transfer.

TABLE 5-15 LIQUID AND GAS PHASE SOURCES AND SINKS

Species	Designation	Sources and Sinks		
		Interphase Gas Transfer	BOD Oxidation	Bacterial Respiration
(a) Liquid Phase, $S^l_{i,n}$				
O_2	$C_{1,n}$	$+K_La(H_1P_{1,n} - C_{1,n})$	$-a' \dfrac{kXC_{4,n}}{K_s + C_{4,n}}$	$-b'X$
CO_2	$C_{2,n}$	$+K_La(H_2P_{2,n} - C_{2,n})$	$+a'' \dfrac{kXC_{4,n}}{K_s + C_{4,n}}$	$+b''X$
N_2	$C_{3,n}$	$+K_La(H_3P_{3,n} - C_{3,n})$		
BOD	$C_{4,n}$		$-\dfrac{kXC_{4,n}}{K_s + C_{4,n}}$	
(b) Gas Phase, $S^g_{i,n}$				
O_2	$P_{1,n}$	$-K_La(H_1P_{1,n} - C_{1,n})$		
CO_2	$P_{2,n}$	$-K_La(H_2P_{2,n} - C_{2,n})$		
N_2	$P_{3,n}$	$-K_La(H_3P_{3,n} - C_{3,n})$		

As a typical example, the mass balance equation for dissolved oxygen in the n'th stage reactor is:

$$\frac{dc_{1,n}}{dt} = \frac{Q}{V_n^1}(C_{1,n-1} - C_{1,n}) + K_L a(H_1 P_{1,n} - C_{1,n}) \tag{51}$$

$$- \left[a' \frac{kXC_{4n}}{K_s + C_{4n}} \right] + b'X$$

Solving for the dissolved oxygen concentration in the n'th stage at steady state yields:

$$C_{1,n} = \frac{\frac{Q}{V_n^1} C_{1,n-1} + K_L a H_1 P_{1,n} - \left[a' \frac{kXC_{4n}}{K_s + C_{4n}} + b'X \right]}{\frac{Q}{V_n^1} + K_L a} \tag{52}$$

Other equations for the concentrations of other species can be obtained similarly.

In addition to the seven equations indicated in Table 5-15, two more equations are needed to complete the equation set. One is for the evaluation of pH. Assuming that the only significant source of alkalinity is carbonaceous alkalinity, and that the pH is in the neutral range, then all the alkalinity occurs substantially as bicarbonate alkalinity. For the first dissociation reaction of carbonic acid, the following equations can be obtained:

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} \cong \frac{(H^+)(Alk)}{(CO_2)} = \frac{(H^+)(Alk)}{C_{2,n}}$$

So

$$pH_n = pK_1 + \log(Alk) - \log(C_{2,n}) \tag{53}$$

The final equation is the continuity condition in the gas phase. The gas flow rates, G_n, may vary from stage to stage, so a continuity condition is required to calculate the gas flows. In the present practice of staged covered reactors for HPOAS, negligible head loss usually occurs in the gas flow from stage to stage; the total pressure in the gas phase of each stage is, therefore, a constant, P_T, and equal to the sum of the partial pressure of the individual gases present, i.e.

$$P_{1,n} + P_{2,n} + P_{3,n} = P_{Tn} = P_T \qquad (54)$$

For the UNOX system, oxygen gas enters the first stage at a slight pressure (1-4 inches water column gauge) and flows from stage to stage with enough velocity to prevent gas backmixing[30].

Equations (53), (54) and those partially described in Table 1-1 make up a total of nine equations, five for the liquid phase and four for the gas phase, to solve for the nine key parameters discussed previously. Given all the necessary [illegible]cients in these equations, the steady state condition of the key parameters can be determined for each stage. In general these calculations may be done for the following purposes:

1. To determine the number of stages required for a certain treatment efficiency and the capacity of each stage;
2. To match the supply with the demand of oxygen in each stage and thus determine the gas flow rate and the capacity of the aerators;
3. To select the optimal combination of various design components, e.g. the economic tradeoff between increasing gas flow and increasing aerator power to obtain a desirable mixed liquor dissolved oxygen concentration.

The use of this model for design requires considerably more information than has been published. Some calculations have been made for our examples and they are given later. To make the actual designs for our examples we have relied on the past experience of Union Carbide Corporation treating similar wastewaters using their UNOX system. We are much indebted to Union Carbide.

5.5.6 Summary of Design Procedures

The design of a High Purity Oxygen Activated Sludge system using past experience includes sizing the oxygenation basins and clarifiers and determining the oxygen and electric power requirements. The procedures are outlined in the following paragraphs.

Oxygenation Basins

1. Determine BOD (mg/l) applied to bioreactors.

2. Determine F/M (applied) and MLVSS (mg/l) from field experience or pilot studies.

3. Calculate hydraulic retention time (RT_Q) by using the following equation:

$$RT_Q \text{ (hrs)} = \frac{\text{BOD (mg/l)} \times 24 \text{ (hrs/day)}}{\text{MLVSS (mg/l)} \times \text{F/M [lb BOD/(lb MLVSS)(day)]}} \qquad (55)$$

4. Calculate the total volume of the oxygenation basins (V) which is the product of RT_Q and Q (hydraulic feed rate).

5. Calculate the total surface area (A) by assuming an economic water depth, d, in the oxygenation basin, A = V/d.

6. Determine the total number of stages to provide the area, each stage being a square in cross section.

7. Design the overall configuration of the oxygenation basins, including number of trains and number of stages in each train.

It should be noted that the use of F/M ratio can actually be related to the biokinetic model discussed, as shown in the following equation:

$$\frac{1}{\theta_c} = Y \text{ (F/M)(BOD removal \%)} - k_d$$

Such correlation of different design techniques has been discussed by Sherrard[19].

Recirculation and Cooling of Mixed Liquor

1. Calculate the BOD removed in mg/l

2. Calculate the temperature rise of mixed liquor on the basis of 1°F temperature rise per 165 mg/l BOD removed.

3. Assume the temperature of the influent wastewater to be 90°F, and that the temperature of mixed liquor is not to exceed 104°F. Calculate the heat removal rate, in Btu/hour for example, to be achieved by a heat exchanger or equivalent.

4. Determine the required area of heat exchanger on the basis of heat removal rate, wet bulb temperature and heat exchange coefficient.

Clarifiers

1. Assume the overflow rates for Steps 1 and 2 to be 700 and 400 gpd/sq ft respectively.

2. Calculate the total surface area by dividing the hydraulic flow rate to the clarifiers by the overflow rate.

3. Determine the diameter of the clarifiers by considering the number of clarifiers to be preferably more than one.

4. Select the depth of clarifiers, usually in the order of 15 ft.

Oxygen and Electric Power Requirement

1. Calculate BOD removed in each step in pounds of BOD per day.

2. Determine the oxygen requirement in terms of pounds of oxygen required per lb of BOD removed.

3. Determine average oxygen utilization efficiency for each step according to the feed BOD concentration.

4. Calculate the amount of oxygen to be transferred in lbs of oxygen per day.

5. The energy required for oxygen transfer is about 191 kw-hr per ton of oxygen transferred, and that for oxygen generation is about 330 kw-hr per ton of oxygen generated (partly as drive steam and partly as electricity).

5.5.7 Example 1. Moderate Strength Wastewater.

A feed of 0.3 x 10^6 gals/day at 2,500 mg/l BOD means an application of 6,255 lb BOD/day. This and other design information is tabulated in Table 5-16. The chosen F/M ratio is 0.8. The chosen MLVSS is 4,000 mg/l. The hydraulic residence time from Equation (55) is:

$$\frac{(2{,}500)(24)}{(4{,}000)(0.8)} = 18.75 \text{ hours}$$

The aeration basin volume is 0.23 x 10^6 gals = 31,200 ft^3. This is shown in Figures 5-13 and 5-14. A single train, two-step basin has been chosen.

The temperature rise is

$$\frac{2{,}500 \text{ mg BOD/l}}{165} = 15°\text{F}$$

and cooling is not required.

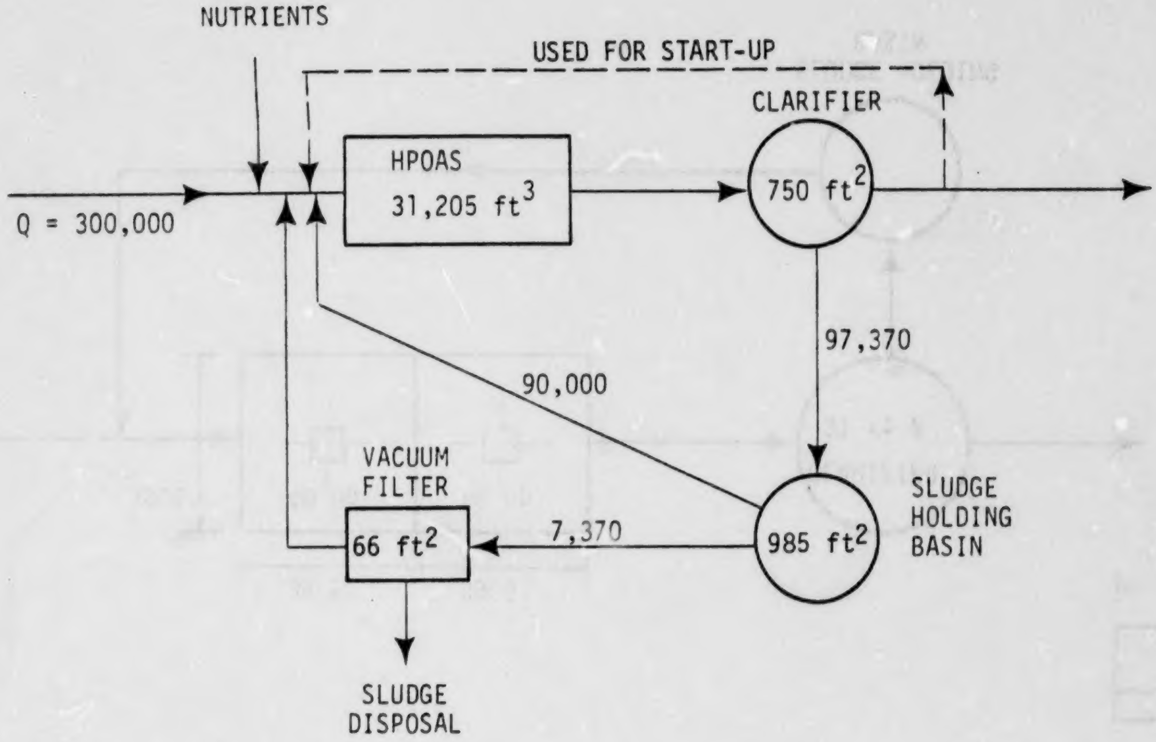
TABLE 5-16. DESIGN OF THE HPOAS SYSTEM, EXAMPLE 1[a]

Design Basis	
Flow, 10^6 gal/day	0.3 (1,671 ft^3/hr)
Phenols, mg/l	300-500
BOD_5, lbs/day	6,255
BOD_5, mg/l	2,500
COD, mg/l	3,000
COD/BOD_5	1.2
Influent suspended solids, mg/l	Negligible
Influent wastewater temperature, °F	90°F
pH	Adjusted as required
Nutrients	Phosphorous to be added
Required effluent BOD, mg/l	45
System Design	
Retention time, hrs (based on feed flow)	19
MLSS, mg/l	5,000
MLVSS, mg/l	4,000
Sludge recycle rate, %Q	30
F/M ratio, lbs BOD_5/(lb MLVSS)(day)	0.8
Average DO level, mg/l	5.0
Oxygen supplied, tons/day	5
Average oxygen utilization efficiency, %	75
Secondary clarifier overflow rate, gal/(day)(ft^2)	400
Recycle suspended solids concentration, wt %	2.0
Effluent soluble BOD_5[b], mg/l	45
Utility Requirements	**Oxygenation Motors**
Operating Energy:	
Brake HP	58
Connected Load:	
Nameplate HP	80
Nameplate HP (stagewise)	40/40

---

[a] information supplied by Union Carbide on the basis of assumptions provided by WPA.

[b] Used as basis for determining oxygen requirement.


NUTRIENTS
USED FOR START-UP
Q = 300,000
HPOAS
31,205 ft³
CLARIFIER
750 ft²
97,370
90,000
VACUUM
FILTER
66 ft²
7,370
985 ft²
SLUDGE
HOLDING
BASIN
SLUDGE
DISPOSAL

ALL FLOWS IN GAL/DAY

Figure 5-13. Schematic flow diagram of high purity oxygen activated sludge (HPOAS) system, Example 1.

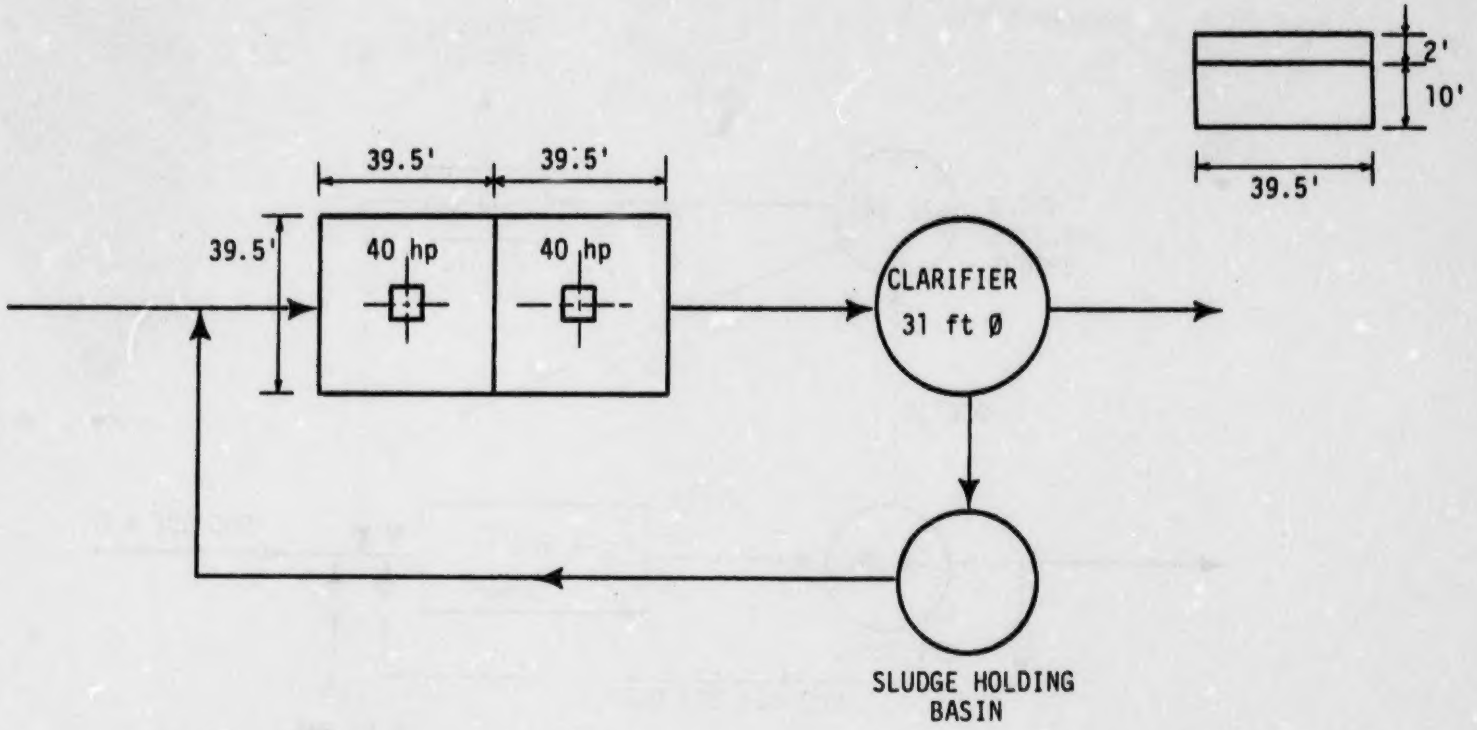

39.5'
39.5'
39.5'
40 hp
40 hp
CLARIFIER
31 ft Ø
SLUDGE HOLDING
BASIN
2'
10'
39.5'

Figure 5-14. Configuration of HPOAS system, Example 1.

The clarifier is sized for 400 gals/(day)(ft^2).

The oxygen requirement is assumed to be 1.22 lb O_2/lb BOD removed, so the oxygen required is:

$$(1.22)(6{,}255 \text{ lb BOD/day}) = 7{,}631 \text{ lb/day}$$

With an assumed utilization efficiency of 75%, the oxygen supplied is:

$$10{,}175 \text{ lb/day} = 5 \text{ tons/day}$$

The oxygenation motor brake horsepower is based on 7.3 lb O_2/hp-hr; 200 kw-hrs/ton oxygen supplied.

The sludge growth rate, based on UNOX experience, is 0.22 lb TSS/lb BOD removed, or 1,376 lb TSS/day. If the clarifier yields an underflow of 2% solids, the wasting rate is 67,430 lb water/day or 7,370 gallons/day. The 24-hour sludge holding basin has a capacity of 7,370 gallons = 985 ft^3. At 3 lb dry weight/(ft^2)(hr), the active filter area for operation 7 hrs/day is 1,376 lb sludge/(21 lb/ft^2) = 66 ft^2.

5.5.8 Example 2. High Strength Wastewater.

For this example the flow is 0.17 x 10^6 gal/day at 18,000 mg/l BOD. Two steps have been used, each giving 95% removal of BOD. In each step a MLVSS concentration of 4,000 mg/l is used. In Step 1, with the higher BOD loading, F/M has been taken as 0.5; in Step 2 F/M has been taken as 0.3. The design basis is listed in Table 5-17.

The Aeration Basins

From Equation (55) the hydraulic residence time in Step 1 is:

$$\frac{(18{,}000)(24)}{(4{,}000)(0.5)} = 216 \text{ hrs}$$

and in Step 2 is 18 hours.

The aeration basin volumes are 1.5 x 10^6 gal = 202,000 ft^3 and 0.13 x 10^6 gals = 17,000 ft^3. These volumes are shown on Figures 5-15 through 5-17. Single train basins have been chosen; four stages in Step 1 and two stages in Step 2.

TABLE 5-17. DESIGN OF THE HPOAS SYSTEM

EXAMPLE NO. 2[a]

Design Basis	
Flow, 10^6 gal/day	0.17 (947 ft^3/hr)
Phenols, mg/l	3,000 - 5,000
BOD$_5$, lbs/day	25,520
BOD$_5$, mg/l	18,000
COD, mg/l	25,000 - 30,000
COD/BOD$_5$	1.5
Influent suspended solids, mg/l	Negligible
Influent wastewater temperature, °F	90°F
pH	Adjusted as required
Nutrients	Phosphorous to be added
Required effluent BOD, mg/l	45

System Design	Step 1	Step 2
Flow, Q(10^6 gal/day)	0.17	0.17
Influent temperature °F	90	101
Retention time, hrs (based on feed flow)	216	18
MLSS, mg/l	5,000	5,000
MLVSS, mg/l	4,000	4,000
Sludge recycle rate, %Q	14	30
Recycle for cooling, %Q	640	-
F/M ratio, lbs BOD$_5$/(lb MLVSS)(day)	0.5	0.3
Average DO level, mg/l	5.0	5.0
Oxygen supplied, tons/day	31	2
Average oxygen utilization efficiency, %	70	65
Secondary clarifier overflow rate, gal/(day)(ft^2)	700	400
Recycle suspended solids concentration, wt %	2.0	2.0
Effluent soluble BOD$_5$[b], mg/l	900	45

Utility Requirements	Oxygenation Motors		
	Step 1	Step 2	Total
Operating Energy:			
Brake HP	311	20	331
Connected Load:			
Nameplate HP	385	30	415
Nameplate HP (stagewise)	125/100/100/60	15/15	

---

[a] Information supplied by Union Carbide on the basis of assumptions provided by EPA.

[b] Used as basis for determining oxygen requirement.

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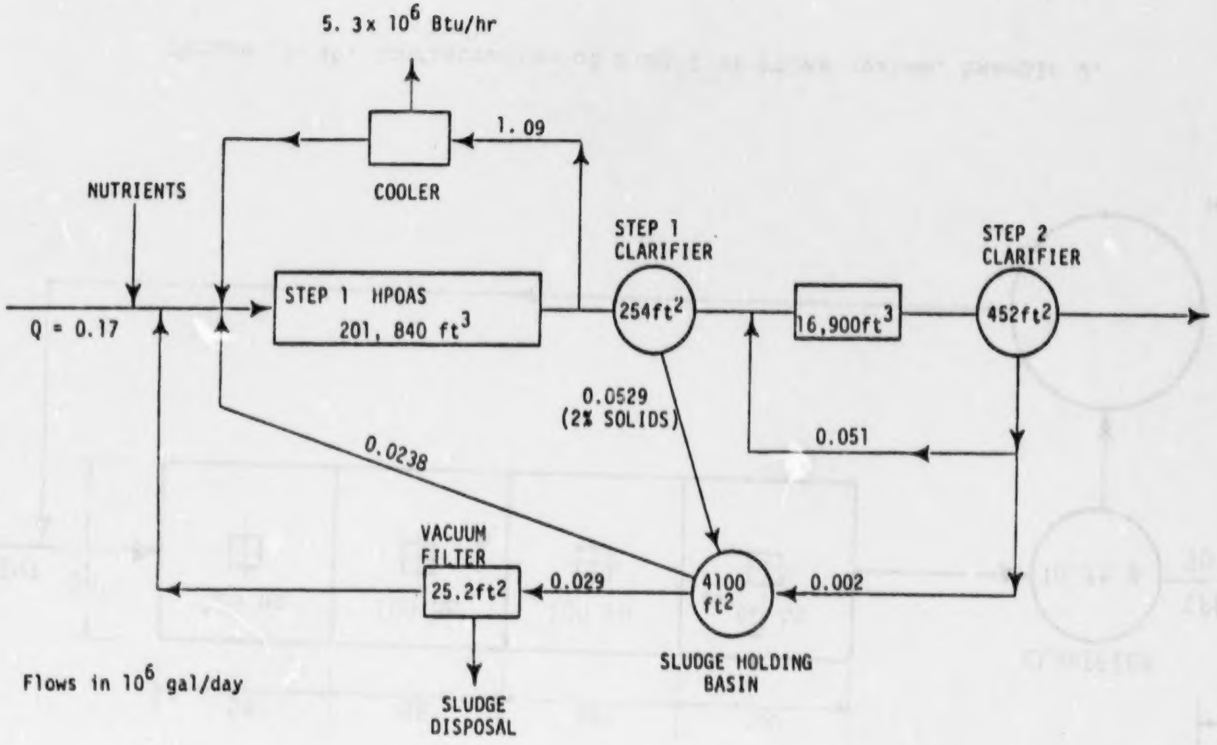
5. 3x 10^6 Btu/hr
1. 09
NUTRIENTS
COOLER
STEP 1 CLARIFIER
STEP 2 CLARIFIER
STEP 1 HPOAS
201, 840 ft^3
Q = 0.17
254ft^2
16,900ft^3
452ft^2
0.0529
(2% SOLIDS)
0.051
0.0238
VACUUM FILTER
25.2ft2
0.029
4100 ft2
0.002
SLUDGE HOLDING BASIN
Flows in 10^6 gal/day
SLUDGE DISPOSAL

Figure 5-15. Schematic flow diagram of high purity oxygen activated sludge (HPOAS) system, Example 2.

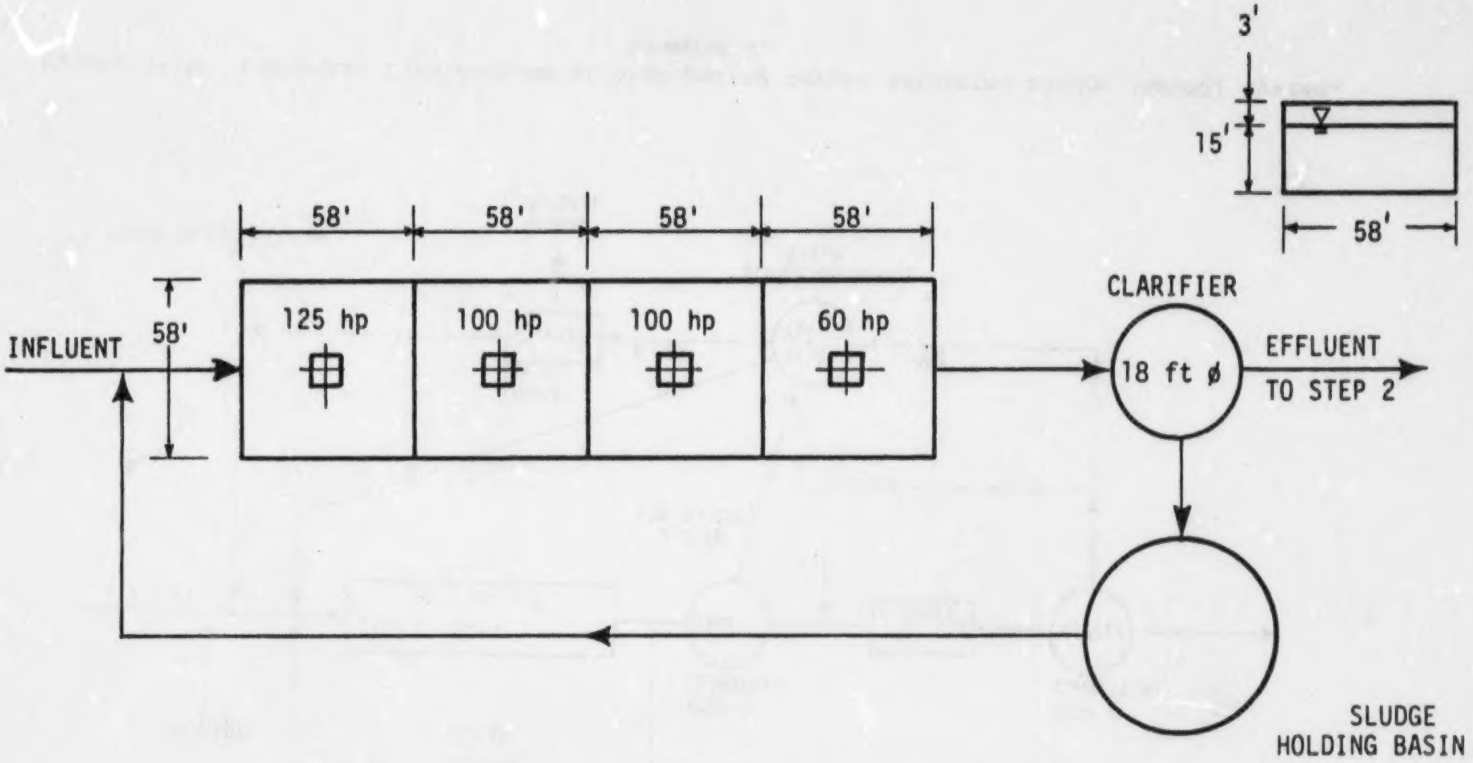
3'
15'
58'
58'
58'
58'
58'
INFLUENT
58'
125 hp
100 hp
100 hp
60 hp
CLARIFIER
18 ft ø
EFFLUENT
TO STEP 2
SLUDGE
HOLDING BASIN

Figure 5-16. Configuration of Step 1 of HPOAS system, Example 2.

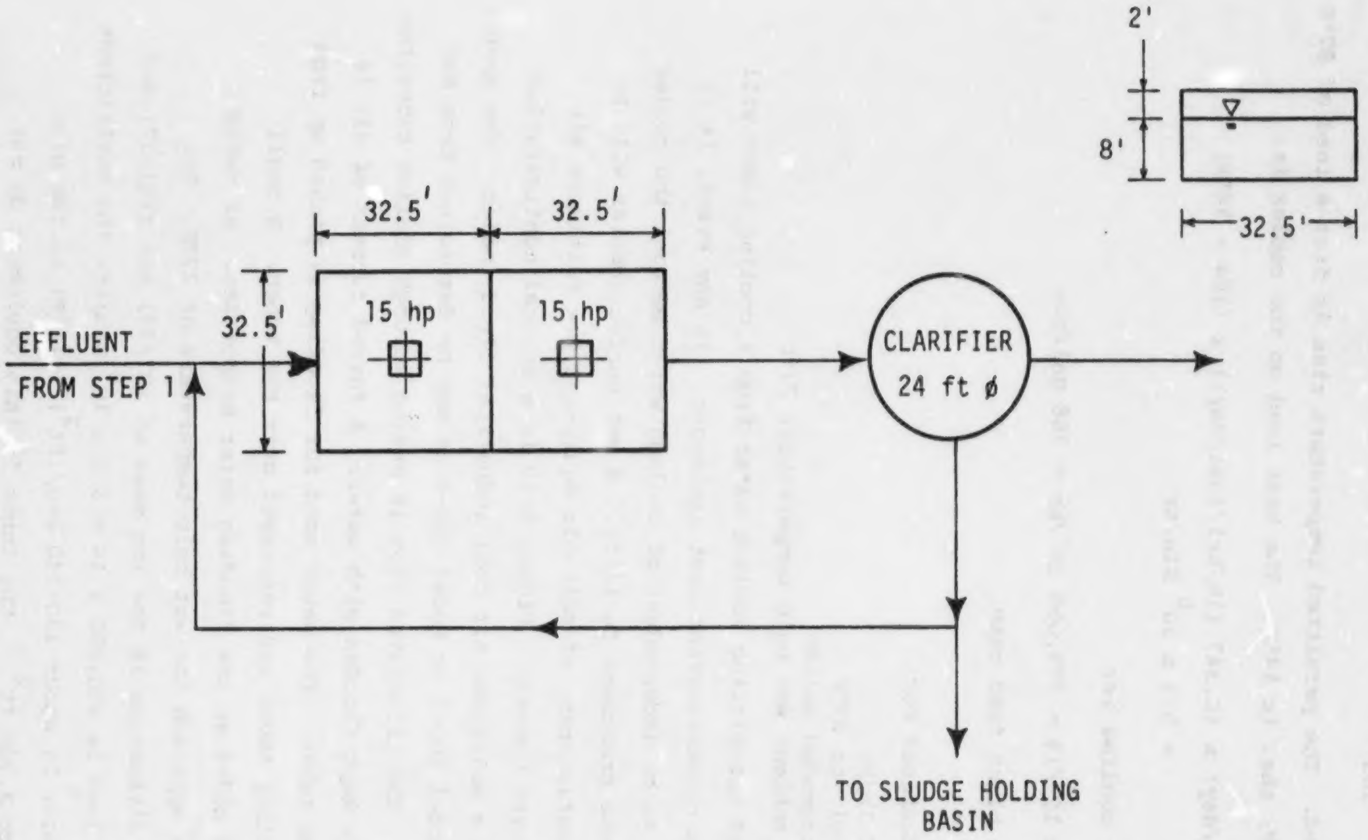
EFFLUENT
FROM STEP 1
32.5'
32.5'
32.5'
15 hp
15 hp
CLARIFIER
24 ft ø
TO SLUDGE HOLDING
BASIN
2'
8'
32.5'

Figure 5-17. Configuration of Step 2 of HPOAS system, Example 2.

Cooling Load

The expected temperature rise in step 1 is:

$$\frac{(18{,}000 - 900)\ \text{mg/l BOD}}{165} = 104°\text{F}$$

so cooling is required. The permitted temperature rise is from a feed of 87°F to a maximum of 101°F; that is 14°F. The heat load on the cooler is:

$$(0.17 \times 10^6\ \text{gal/day}) \times (0.347\ (\text{lb/hr})/(\text{gal/day})) \times (104 - 14°\text{F})$$
$$= 5.3 \times 10^6\ \text{Btu/hr}$$

The recycle rate for cooling is:

$$5.3 \times 10^6/14 = 379{,}000\ \text{lb /hr} = 758\ \text{gal/min}$$

which is 640% of the plant feed rate.

Cooler Design

The cooler is designed for

- 400,000 lb/hr
- range 101° to 87°F
- high suspended solids
- design ambient wet bulb temperature, 77°F

It is not likely that circulating cooling water from a cooling tower will be cold enough for a countercurrent heat exchanger. In any event, it is probably convenient to be independent of cooling water because the cooler will be near the waste treatment facility. A wet surface cooler will be used. Among the manufacturers of suitable equipment are Baltimore Air Coil and Niagara Blower Company. Figure 5-18 is a typical configuration.

Consider first a Baltimore Air Coil industrial fluid cooler. The specified equipment is Model 200-3 or Model 300-1 as may be determined from BAC Bulletin S 404/1-0. The circulated flow is passed through cooling tubes,the outside of which are kept flooded with water. A forced current of air is also passed over the tubes. The water used for flooding is picked up from a pan below the cooling tubes and resprayed over the tubes. A small amount of makeup is added as the flooding water evaporates. At design, flooding water will approach the wet bulb temperature of 77°F. The design temperature difference is the log mean of (87-77) and (101-77) and equals 16.0°F; the load is 400,000 x 14 = 5.6×10^6 Btu/hr; the coefficient in this type of cooler is about 130-140 Btu/(ft^2)(hr)(°F) so the area required is 2,500 to 2,700 ft^2. The tubes in this equipment do not

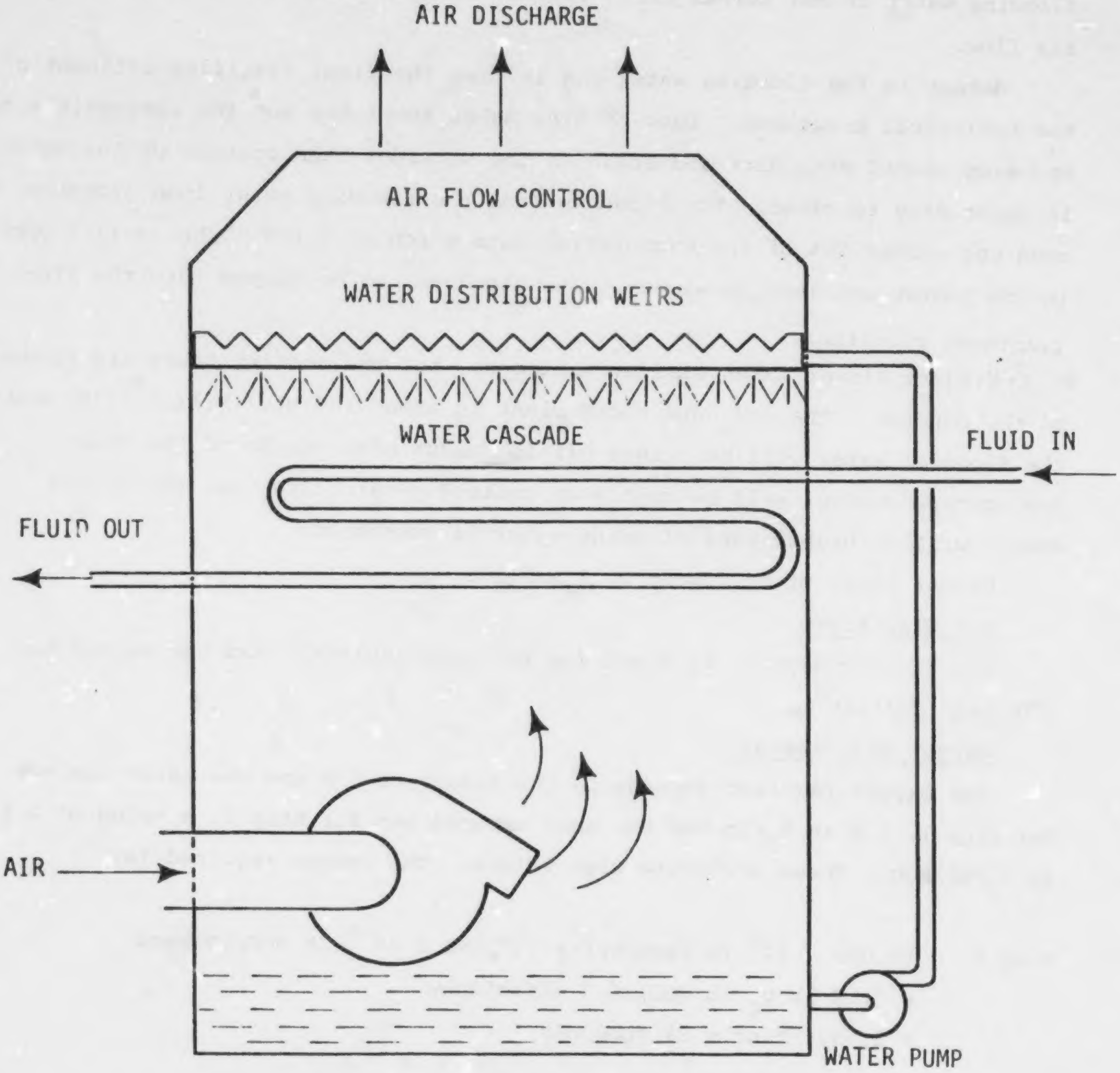
AIR DISCHARGE
AIR FLOW CONTROL
WATER DISTRIBUTION WEIRS
WATER CASCADE
FLUID IN
FLUID OUT
AIR
WATER PUMP

Figure 5-18. Cooler schematic.

have fins. Dry tubes with forced air will have a heat transfer coefficient of not more than 15 Btu/(hr)(ft^2)(°F) and even on the coldest winter days the flooding water is not turned off. Control of temperature is by dampers in the air flow.

Makeup to the flooding water pan is from the final clarifier effluent of the biological treatment. Lack of fins makes the tubes not too susceptible to becoming coated with dirt and scale on the outsides; the outside of the tubes is quite easy to clean. The blowdown from the flooding water loop probably need not exceed 50% of the evaporation rate which is 5,600 lb/hr (= 11.2 gpm) in the summer and less in winter. The blowdown can be dumped into the biotreatment clarifier.

Niagara Blower makes similar equipment, but the cooling tubes are finned on the outside. The dry tube coefficient is about 100 Btu/(hr)(ft^2)(°F) and the flooding water will be turned off for about nine months of the year. Temperature control will be mostly by control of air flow, but the blower energy will be higher when flooding water is turned off.

Either piece of equipment will suffice.

The Clarifiers

The first clarifier is sized for 668 gal/(day)(ft^2) and the second for 376 gal/(day)(ft^2).

Oxygen Requirement

The oxygen required depends on the values of F/M and the ratio COD/BOD. For Step 1, 1.8 lb O_2/lb BOD has been assumed and for Step 2, a value of 2.1 lb O_2/lb BOD. These are quite high values. The oxygen required is:

Step 1. (0.059 x 10^6 lb feed/hr) x (17,100 x 10^{-6} lb BOD/lb feed
x (1.8 lb O_2/lb BOD)/0.7 efficiency
= 2,590 lb/hr = 31 tons/day

Step 2. (0.059)(855)(2.1)/0.65 = 163 lb/hr = 2 tons/day

The average oxygenation motor efficiency is 8.2 lb O_2 supplied/hp-hr.

Sludge

The total sludge production is about
(24,244 lb BOD removed/day) x (0.22 lb sludge/lb BOD) = 5,300 lb/day

The total waste sludge water rate at 2% solids is 0.26×10^6 lb/day = 0.031×10^6 gal/day. The waste sludge rate is 0.029×10^6 gal/day in Step 1 and 0.002×10^6 gal/day in Step 2. The sludge holding basin for 24 hours is 31,000 gallons = 4,100 ft^3. The active filter area is 252 ft^2 for operation 7 hrs/day.

5.5.9 Use of the Model

Some calculations were made on the model described in Section 5.5.5 to find if the two examples could be described. There is not enough information to use the model properly, but it appears to promise a method of correlating an operating plant. At this time the model requires too much data to be useful for design.

The constants used were as follows:

For both examples we used the biokinetic constants used for air activated sludge:

k = 1 g soluble BOD/(g.MLVSS)(hr)

k_d = 0.033 hr^{-1}

Y = 0.37 g.MLVSS/g.BOD removed

K_s = 266 mg.BOD/l

The Henry's law constants were:

O_2; $H = (1.779 \times 10^6)/(7{,}241\ t^{0.545})$

CO_2; $H = (2.446 \times 10^6)/(64.58\ t^{0.988})$

N_2; $H = (1.557 \times 10^6)/(27{,}300\ t^{0.363})$

where t is in ^oC, c is in mg/l, and P is in atm.

The respiratory quotient from Equation (50) was taken as 1.

The oxygen requirements were taken from the examples:

Example 1: a' = 1.22, b' = 0.0042

Example 2: a' = 1.80, b' = 0.0042

The recycle and sludge conditions also were taken from the examples.

We found that in Example 1 a possible simulation was obtained with K_La (the gas transfer rate in Equation (45)) equal to 14 in Step 1 and 6 in Step 2. The oxygen transfer rate depends on the gas phase concentration and on the aerator horsepower. The model gave negative oxygen concentrations in the liquid in Step 1 because the equations permit it. Removals of BOD were higher than expected. Modification of the model to show possible oxygen starvation may help. However, we used the plant design to find gas transfer rates for a given set of biokinetic constants which may not be correct. If the biokinetic constants are wrong, the model is probably so complex that it cannot be used to find them. The biokinetic constants must be determined independently.

In Example 2 we modeled the first stage only using:

Step 1: $K_La = 44$
Step 2: $K_La = 31$
Step 3: $K_La = 25$
Step 4: $K_La = 12$

The model gave very high BOD removals and sludge concentrations not over 500 mg/l. Other values were simulated. It seems that the kinetics were too fast to really simulate the design of Example 2.

5.6 Trickling Filters

A trickling filter is a method of obtaining a high concentration of bacteria by allowing them to grow on the solid surface of grid-like packing while wastewater trickles in a thin film over the surface. An important cost in activated sludge biological oxidation is the cost of supplying oxygen. In a trickling filter, water and not air, is pumped and the energy required is much lower than in an activated sludge process. The use of dual biological processes (using a combination of trickling filter and activated sludge) for industrial wastewater treatment is not new[33]. Success in the treatment of wastewaters from organic chemical manufacturing, petrochemical refining and meat processing industrials has been reported[33,46]. In most of the reported cases the water contaminants of primary concern have been phenols and BOD, and they were successfully removed by combining the desirable attributes of a trickling filter and an activated sludge process into the most economical treatment system[33].

Trickling filters and experience with them are classified according to the hydraulic loading and the organic loading[51]. Of interest in the treatment of coal conversion wastewaters are:

	Hydraulic Loading $gal/(min)(ft^2)$	Organic Loading $lb\ BOD/(day)(10^3 ft^3)$
Super rate filters with synthetic media	0.25 to 1.5*	up to 300
Roughing filters	1.0 to 3.0	100 plus

~~*not~~

---

*not including recirculation

In general trickling filters will not give as clean an effluent as an activated sludge process. With high organic loadings, the fraction of the BOD removed can be quite low; as low as 40%. With wastewaters from coal conversion, the proper place for a trickling filter is as a roughing filter ahead of the activated sludge plant. However, the use of a trickling filter on wastewaters as concentrated as those from coal conversion has not been reported and must be regarded as experimental. Although design procedures are given below, they are based on correlations of trickling filter performance on quite different wastes. The designs will serve to produce an experimental trickling filter, not to build equipment that is certain to perform to specification.

5.6.1 Design of Trickling Filters

Several different correlations have been used for trickling filters[51]. The formula most applicable for our purposes is the modified Germain formula[51]:

$$\frac{L_e}{L_a} = \exp\left(-\frac{KD\theta}{J^n}\right) \qquad (56)$$

where

L_e = BOD of the effluent, mg/l
L_a = BOD of the influent, mg/l
K = treatability factor
D = fill depth, ft
θ = temperature factor, = $1.035^{(T-20)}$, where T = water temperature in °C
J = water flux through the filter, gal/(min)(ft^2)
n = medium factor

The treatability factor K is a measure of the susceptibility of the wastewater to biological treatment. The medium factor, n, is a function of the character of the medium, that is, its specific surface area and geometry, etc., which can affect the contact time between water and biological mass on the surface of the medium.

Equation (56) is a correlating formula, not a design formula. The term D/J has the dimensions of time. Equation (56) relates the fractional removal of BOD to the contact time on the filter. There is no expression for the effect of feed concentration on the fractional removal in a given filter.

The treatability factor, K, lumps together the concentration and nature of the waste. K must be determined experimentally. Experience is that K generally lies in the range 0.01 to 0.045 for wastewaters like those from coal conversion. The factor, n, is generally close to 0.5.

5.6.2 Example 1. Moderate Strength Wastewater

Example 1 is a wastewater from a demonstration plant of 0.3×10^6 gal/day 2,500 mg/l BOD. In Table 5-18 some calculations are shown for different values of K and for n = 0.5. The temperature is taken to be 30°C; $\theta = 1.41$. The range of possible values of K is wide enough to make it impossible to suggest a design. Experiment is required to evaluate K.

If even half of the influent BOD is removed, the aerators in a following air activated sludge plant can be reduced by 72 hp, saving 0.47×10^6 kw-hrs/yr, or about $14,000/yr. Assuming that it is economical to invest five times this saving, that is $70,000 in a trickle filter, it is clear that a trickle filter should be investigated. The cost is about $\$10/\text{ft}^3$.

5.6.3 Example 2. Trickle Filter on Recycle with a High Strength Wastewater

Our second example is high strength wastewater having 18,000 mg BOD/l. We have not considered a trickling filter for this water since the concentration is so high as to be, most probably, toxic. However, in designing a high purity oxygen activated sludge plant for this water, it was found to be necessary to recycle 640% of the feed flow for cooling. The recycle contains about 5,000 mg/l MLSS but this will most probably not render it unfit to feed to a trickling filter. Rather than using the flow circuit shown in Figure 5-15, the circuit shown in Figure 5-19 can be used. The recycle is mixed with the feed and applied to a trickling filter. The mixed feed to the trickling filter is 1.26×10^6 gals/day at 3,200 mg BOD/l. For n=0.5 and $\theta=1.41$ some calculations are shown in Table 5-19. The filter should probably be 30,000 ft^3 to hold the organic loading down to the level of experience.

This trickling filter must also supply cooling. Packing used in a trickling filter is also usable in a cooling tower and a forced draft cooling tower was designed for this service[52]. A generous volume of packing was 14' x 14' x 5' high = 980 ft^3. A trickling filter thirty times this size is most likely to provide adequate cooling without a forced draft. It will be necessary to support the fill above ground level to provide space for air to enter at the bottom. It will also be necessary to provide louvers so that air entry can be reduced in cold weather to avoid excessive cooling.

TABLE 5-18 TRICKLING FILTER CALCULATIONS FOR EXAMPLE 1

0.3 x 10^6 gal/day at 2,500 mg BOD/l; 6,250 lb BOD/day

Filter				Organic Loading	Hydraulic Loading	Percent Removal $1 - L_e/L_a$		
Diam. (ft)	Area (ft^2)	Depth (ft)	Vol. (ft^3)	lb BOD/(day)($10^3 ft^3$)	(gpm/ft^2)	K=0.045	K=0.02	K=0.01
11.2	100	30	3,000	2,083	2.1	73%	44%	25%
13.8	150	20	3,000	2,083	1.4	66	38	21
16.0	200	15	3,000	2,083	1.0	60	25	13
13.8	150	40	6,000	1,040	1.4	88	61	38
16.0	200	30	6,000	1,040	1.0	84	57	34
19.5	300	20	6,000	1,040	0.69	78	49	29
16.9	225	40	9,000	694	0.93	93	89	44
19.5	300	30	9,000	694	0.69	90	64	40
23.9	450	20	9,000	694	0.46	85	56	34
21.9	375	40	15,000	417	0.56	97	78	53
25.2	500	30	15,000	417	0.42	95	73	48
30.9	750	20	15,000	417	0.27	91	66	42

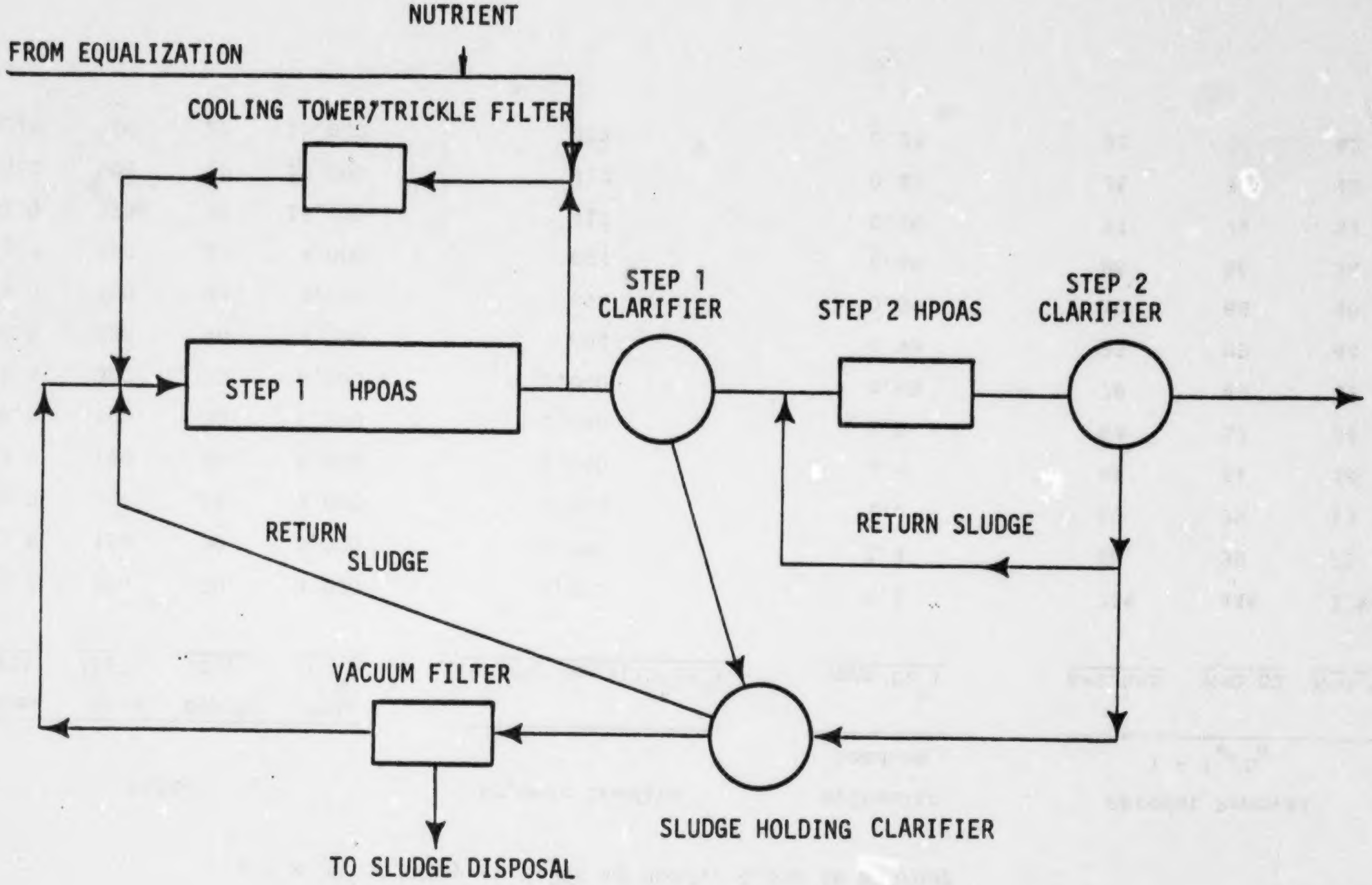
NUTRIENT
FROM EQUALIZATION
COOLING TOWER/TRICKLE FILTER
STEP 1 HPOAS
STEP 1 CLARIFIER
STEP 2 HPOAS
STEP 2 CLARIFIER
RETURN SLUDGE
RETURN SLUDGE
VACUUM FILTER
SLUDGE HOLDING CLARIFIER
TO SLUDGE DISPOSAL

Figure 5-19. Activated trickling filter-high purity oxygen activated sludge system (ATF-HPOAS) for Hygas plant.

TABLE 5-19 TRICKLING FILTER CALCULATIONS FOR EXAMPLE 2

1.26×10^6 gal/day at 3,200 mg BOD/l; 33,600 lb BOD/day

Filter				Organic Loading	Hydraulic Loading	Percent Removal $1 - L_e/L_a$		
Diam. (ft)	Area (ft^2)	Depth (ft)	Vol. (ft^3)	lb BOD/(day)($10^3 ft^3$)	(gpm/ft^2)	K=0.045	K=0.02	K=0.01
30.9	750	40	30,000	1,120	1.2	90%	64%	40%
35.7	1,000	30	30,000	1,120	0.88	87	59	36
43.7	1,500	40	60,000	560	0.58	96	77	52
50.5	2,000	30	60,000	560	0.44	94	72	47

5.7 Anaerobic Biological Destruction

In the anaerobic biological treatment processes, organic constituents of the wastewater are converted to methane and carbon dioxide. General explanations are given in References 32 and 39. The major advantages of anaerobic over aerobic biological treatment are:

(1) Less sludge growth will be produced in the anaerobic process, about 0.05 to 0.2 pounds suspended solids per pound BOD_L, while the corresponding figure for the aerobic process may be as high as 0.4. Sludge production varies with the nature of organic constituents and the mean cell residence time, θc.

(2) The problem of biological sludge disposal and the requirement of a nutrient, phosphorus in this case, will be significantly reduced.

(3) Elimination of aeration results in significant savings in energy and operating costs.

(4) The methane gas produced can serve as a source of fuel.

On the other hand, the major disadvantages of anaerobic processes lie in their relatively high susceptibility to upsets due to toxicants or shock loads and the lack of field experience with the coal conversion wastewater.

Studies[47] have shown that petrochemical wastewaters may be successfully treated by anaerobic lagoons in a large-scale pilot plant. Anaerobic filters and contact digesters (i.e. anaerobic activated sludge) provided satisfactory removals when treating dilute wastes in bench-scale studies, but neither unit provided satisfactory removals when tested on a semi-pilot scale with actual wastes. The difference in performance between the lagoons and the other two systems was due to the ability of the lagoons to metabolize volatile acid intermediates. The characteristics of these three anaerobic systems are shown in Table 5-20.

Only limited data are available on the inhibitory effect of certain chemicals found in petrochemical industrial wastewaters. A study[48] showed that for an active methane-producing, unacclimated, domestic digester sludge the 50 percent inhibitory concentration of phenol (based on gas production) was found to be larger than 1,000 mg/l under substrate-limiting conditions, and it ranged from 300 to 1,000 mg/l (averaging about 400 mg/l) under nonsubstrate-limiting conditions. Through acclimation the inhibitory concentration of phenol will increase. Under nonsubstrate-limiting conditions with a phenol concentration

TABLE 5-20. ANAEROBIC SYSTEMS STUDIED

(From Reference 47)

	Submerged Filter	Contact Digester	Open Lagoon
Description	Rock or gravel packed column	Completely mixed vessel	Basin with considerable stratification
Flow pattern	Plug flow	Backmixed	Some wind and wave mixing, thermal turnovers
Biosolids level	High biomass through attached growths	High biomass through settling and return	Low suspended solids, bottom sludge layer
Metabolic pathways	Fermentation and anaerobic respiration	Fermentation and anaerobic respiration	Fermentation, anaerobic respiration, sulfur oxidation, photosynthesis, some aerobic respiration
Retention time	1 to 3 days	1 to 10 days	10 to 100 days
Gas collection	Normally collected	Collected	Gas is released, although a plastic covering with peripheral collection tiles is possible
Temperature control	Not normally practiced	Usually practiced	Unfeasible unless covered and insulated

of about 500 mg/l, the methane-forming activity of the acclimated biomass was found to be about 95 percent of that for the noninhibited.

In a series of packed-bed anaerobic reactors, the effect of four mixed inhibitors, including phenol, formaldehyde, acrylonitrile and ethyl acrylate, was also studied[48]. The mixed inhibitors were found to act synergistically since they were more detrimental to methane formation as a mixture than would have been predicted based on individual chemical inhibition tests.

Acclimation was found[48] to be unsuccessful in a digester-type reactor unless complete mixing was provided. No such problem was observed in the packed-bed type reactor (upflow anaerobic filters). It was also concluded that acclimation in anaerobic systems was at best a slow process and considerable difficulty would likely be experienced in the startup of a full-scale anaerobic process treating an inhibitory waste.

A more recent study[49] on the anaerobic treatment of oil shale retort water reached the following conclusions:

(1) The retort water studied had to be pretreated to remove toxic constituents (ammonia and sulfide) and to add nutrients in which it was deficient (calcium, magnesium and phosphorus) before it could be successfully treated by anaerobic fermentation. Pretreatment included pH adjustment, air stripping and skimming, and nutrient addition.

(2) A digested sludge from a conventional municipal sewage treatment plant was successfully acclimated to the retort water studied.

(3) A major fraction of the organics in the retort water studied was stabilized by conversion to CH_4 and CO_2 by anaerobic fermentation. BOD_5 and COD removal efficiencies were 76-80%. Within the limits of experimental error, the same removal rate was obtained for both BOD_5 and COD.

(4) The effluent from anaerobic fermentation of the retort water studied (BOD_5:530 - 580 mg/l) might be suitable for treatment by conventional aerobic processes.

(5) The growth of the methane formers, which stabilize the organics, is nutrient limited in the retort water studied.

(6) Pretreatment of the retort water removed 49% of the BOD_5. This was probably due to the reduction in solubility of high molecular weight fatty acids at neutral pHs; they precipitate out of solution and do not exert a BOD.

(7) During anaerobic fermantation a major component removed from the retort water studied was fatty acids.

(8) The long hydraulic residence time used in this study (about 50 days) would not be used in practice. Cell recycle, which increases the cell residence and decreases the hydraulic residence time, should be to achieve hydraulic residence times on the order of 2 - 3 days. In this study all recycle was achieved by removing a sample of the digester mixed liquor, centrifuging it at 2,500 rpm for 3 min, and returning the centrate (biological mass) to the digester.

Based on the findings of these recent studies, the following recommenda tionsmay be offered for coal gasification wastewaters:

(1) Experiments on anaerobic fermentation should be conducted with continuously mixed reactors with long mean cell residence time, θc, of probably more than 50 days[49].

(2) Pretreatment procedures, such as those described in other parts of this report, will be required to reduce the concentration of any toxic constituents below the threshold level.

(3) The nutrient requirements of anaerobic fermentation should be established and any nutrient deficiency should be corrected by adding appropriate chemical(s).

(4) It is unlikely that anaerobic fermentation alone can achieve the treatment objective satisfactorily. After the technical feasibility of anaerobic fermentation is established, then the possibility of following anaerobic fermentation by aerobic biotreatment should be evaluated.

5.7.1 Design of Experiments on Anaerobic Fermentation

In general, References 47 and 49 are excellent guides for conducting experiments on anaerobic fermentation. Preliminary design of such experiments is described in the following paragraphs.

A. Reactor Configuration

The reactor should be continuously mixed and heated to maintain a temperature of about 35°C. It should also have provisions for feeding the wastes, withdrawing effluent or samples and collecting and measuring the gaseous products as shown in Figure 5-20. The capacity of the reactor depends on th hydraulic residence time and the volumetric feed rate.

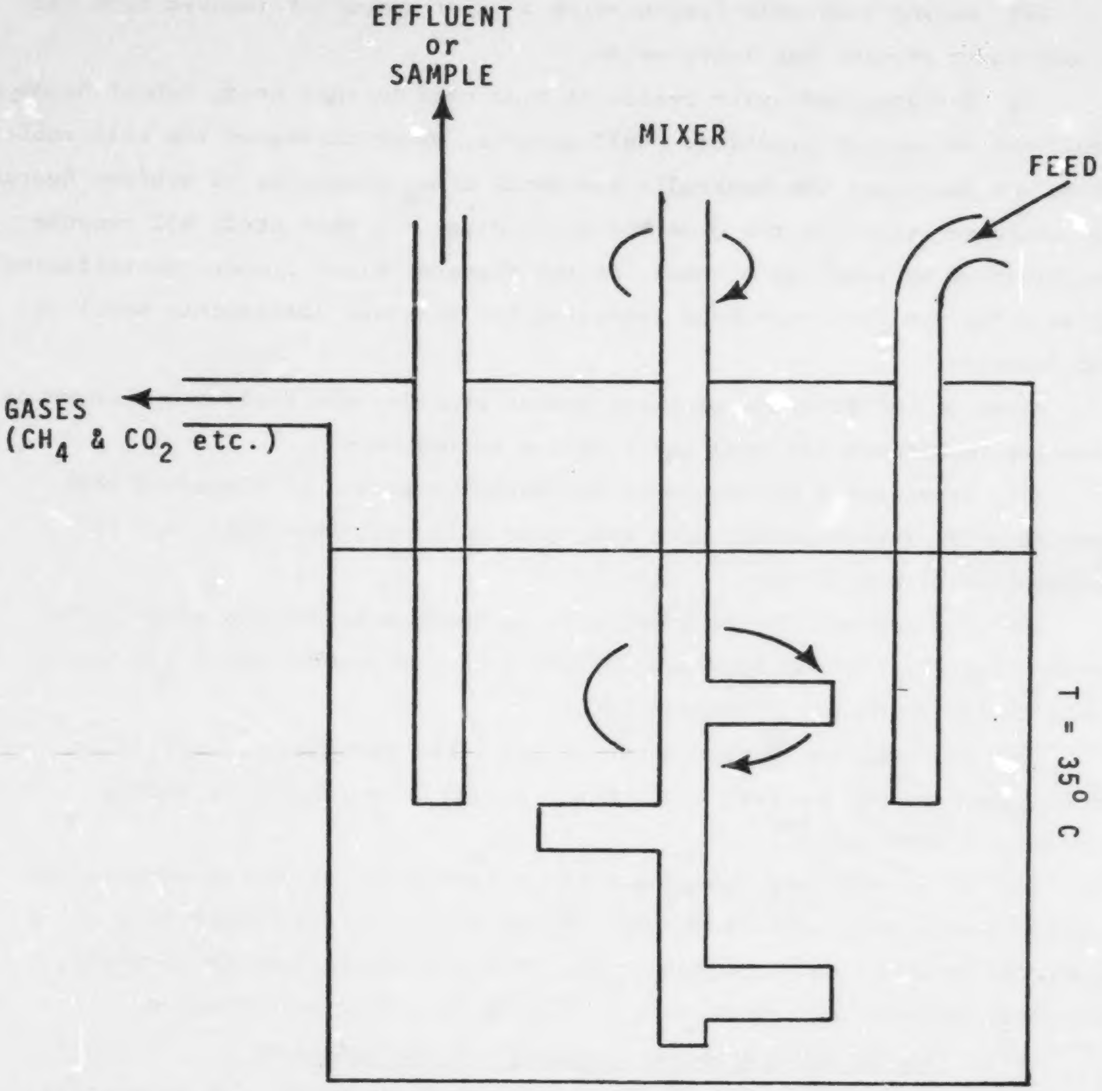
EFFLUENT
or
SAMPLE
MIXER
FEED
GASES
(CH_4 & CO_2 etc.)
T = 35° C

Figure 5-20. Schematic of continuously mixed batch anaerobic digester.

B. Toxicants and Nutrients

For the same chemical there may be an optimal and toxic concentration as shown in Table 5-21. Furthermore, the toxic levels may vary considerably from the listed values because of synergistic or antagonistic effects of other chemical species[50]. However, the values in Table 5-21 may be used to identify potential toxicity, required pretreatment, and nutrient deficiency.

C. Acclimation

If a digested sludge from a conventional municipal sewage treatment plant is used to seed the reactor, the microbes in the digested sludge may be acclimated to coal conversion wastes by incremental additions of coal conversion wastewater to the municipal sludge feed. After each incremental addition, the digester must be monitored until steady state conditions are attained. The parameters used as indicators of a steady state should include volatile suspended solids, volatile acids, and volume and composition of digester gas.

D. Cell Recycle

When it is desired to maintain a short hydraulic residence time and a long cell residence time, the separation and recycle of the active biomass, especially the methane former, will become necessary. Digester failures have frequently been attributed to a population imbalance between acid formers and methane formers. Methane formers are generally more sensitive to environmental conditions and usually grow more slowly than acid formers. The population imbalance usually means a gradual washout of methane formers and eventually a digester failure.

Although it is highly desirable to selectively separate and recycle methane formers, all of the past experience shows that this is not practical. The failures of anaerobic filters and anaerobic activated sludge in treating petrochemical wastewaters[47] might be due to the inability of these systems to selectively separate methane formers from the rest of solids.

The successful cell recycle reported in Reference 44 indicates that centrifugation may be a good technique to separate methane formers from the liquid phase, but may not necessarily be a preferred technique to separate methane formers from acid formers. The following separation techniques are recommended for testing:

- Centrifugation
- Polymer flocculation followed by sedimentation
- Flotation using CO_2

TABLE 5-21 OPTIMUM AND TOXIC LEVELS FOR ANAEROBIC FERMENTATION

(From Reference 49)

Parameter	Optimum Level (a) (mg/l)	Toxic Level (b) (mg/l)
Sodium	230	>4,600
Potassium	390	>3,900
Ammonium (as NH_4)	180	>1,350
Calcium	200	>2,000
Magnesium	120	>1,200
Soluble Sulfide (as S)	(c)	> 200
Nitrogen	(d)	-
Phosphorus	(d)	-

(a) Maximum efficiency from an anaerobic treatment system can be obtained by maintaining the major ions as close to their optimum values as possible.

(b) Toxic levels may vary considerably from the values shown due to synergistic or antagonistic effects of other ions.

(c) At levels lower than 200 mg-S/l, sulfides can have a beneficial effect by precipitating certain toxic heavy metals, e.g., Cu, Zn, Ni, Fe.

(d) Optimum levels of nitrogen and phosphorus have been demonstrated to depend on the growth rate and concentration of organisms present in the system. They are ~ 11% of cell volatile solids weight for N and 2% of cell volatile solids weight for P.

E. Test Parameters

Test parameters may be broadly classified into two types:

1. Operational parameters: BOD, TOC, volatile acids, alkalinity volatile and total suspended solids, volume and composition of digester gas.

2. Toxicity and nutrient parameters: ammonia, sulfide, phosphorus, calcium, magnesium and others.

It has been reported in Reference 49 that a toxicity and a nutrient deficiency problem could be differentiated by comparing total gas production and gas composition. When toxicity was the cause of failure, the gas composition changed significantly; CH_4 decreased and CO_2 and trace gases increased. When the system was nutrient limited, total gas production decreased while gas composition remained constant and comparable to that observed in a properly operating digester.

F. Data Analyses

The behavior of the anaerobic fermentation process may be described by the same biokinetic model used for the air activated sludge process. In other words, its behavior may be summarized by the value of four coefficients: k, K_s, Y and k_d. The same data analyses should be undertaken for anaerobic fermentation as for air activated sludge except that oxygen balance does not apply to the anaerobic process. Values of the four coefficients have been reported in the literature[2] primarily for the anaerobic treatment of municipal sludges.

5.8 The Place of Biological Oxidation

Biological oxidation can be considered to be in competition with solvent extraction and adsorption as a method of removing organic contamination from wastewater. The choice of process will depend on the cost and on the quality of the effluent water.

5.8.1 Cost

Cost estimates for our two examples of activated sludge treatment and a related third example are shown in Table 5-22. The cost of an air activated sludge plant is always higher than the cost of an oxygen activated sludge plant. This is because the slow kinetics with air necessitate much larger basins than are needed for oxygen and the expense of pure oxygen is not high enough to offset it. The cost of the aeration basin is

TABLE 5-22 COST OF ACTIVATED SLUDGE TREATMENT

	Example 1		Example 2		Example 3	
	Air	Oxygen	Air	Oxygen	Air	Oxygen
Flow (10^6 gal/day)	0.3	0.3	0.17	0.17	0.41	0.41
BOD (mg/l)	2,500	2,500	18,000	18,000	9,000	9,000
Capital investment, $\$10^6$	1.5	0.8	6.6	3.2	5.6	3.4
Capital related charges, $\$/10^3$gal	3.3	1.7	25.04	12.1	7.83	4.74
Oxygen, $\$/10^3$ gal	0	0.12	0	1.42	0	0.64
Other charges	0.6	0.18	2.72	2.21	1.10	0.87
Total charges, $\$/10^3$ gal	3.9	2.00	27.76	15.73	8.83	6.25
\$/100 lb BOD	18.8	9.68	18.46	10.46	11.73	8.32

over 70% of the capital cost of an air activated sludge plant. It is also apparent that the correlation for cost is as $/100 lb BOD removed. All the oxygen plants lie close to $10/100 lb BOD. For municipal plants with intake waters having about 200 mg BOD/l it is not true that the cost is proportional to the rate of removal of BOD. This proportionally only holds true for higher concentrations of feed water.

In an earlier study[39] we also found cost to be proportional to the rate of removal of BOD. In that study we used a trickling filter plus faster kinestics and less oxygen consumption than in this report and found $2.50/100 lb BOD removed. The cost, $2.50, is too low. The cost in Table 5-22 is not necessarily correct and needs reevaluation. What does seem to be correct is that cost is proportional to the rate of removal of BOD and that oxygen is preferable to air.

In other parts of this report we show that the cost of solvent extraction is proportional to the rate of water flow and nearly independent of the concentration. Thus, solvent extraction should be considered first for higher concentrations, as in our Example 2. Activated sludge should be considered for lower strength wastewaters and for effluents from solvent extraction. Probably, but we are not certain, solvent extraction is preferable above 2,000 to 4,000 mg BOD/l and activated sludge below 2,000 to 4,000 mg BOD/l.

The cost of solvent extraction increases as the fraction of contaminant removed increases. Solvent extraction is optimum when high fractions removed (perhaps greater than 80%) are not required. In many situations we expect that solvent extraction will be sollowed by adsorption or biological oxidation.

To prevent toxicity most wastewaters must be diluted for biological oxidation to occur. In the usual activated sludge plant this means that the effluent must be at least dilute enough not to be toxic. Furthermore, as has been shown in the examples, sludge residence times large enough to be about twice the minimum and large enough to require a positive sludge recycle will usually result in destruction of more than 90% of the influent BOD. We expect biological treatments to be operated with an effluent BOD in the range 300 to 50 mg/l, usually at the lower level.

The correlation of cost for an absorbtion process is not as simple as for solvent extraction and activated sludge, neither is the design as reliable. The cost depends on both the water flow rate and on the influent concentration. It does seem, however, that low effluent concentrations can be obtained without incurring a high cost. The economical range of concentrations for using adsorption is probably close to the same range for biological oxidation.

Both solvent extraction and adsorption, but not biological oxidation, allow for recovery of the organic matter which may have some value, if only as a fuel.

5.8.2 Quality of Effluent

Biological oxidation removes only biodegradable compounds. However, some additional removal of even nonbiodegradable chemicals occurs by adsorption onto the sludge. It is the experience at several coal conversion pilot plants that wastewaters are satisfactorily biodegradable. Phosphorous, as a nutrient, must be added as biological treatment and an unknown, small, concentration will be left in the effluent. Ammonia as a nutrient will be left over as well, but this is not usually different from the competitive processes.

Since biological treatment converts soluble organic contaminants partly to a sludge, the effluent will have suspended solids in the range 30-100 mg/l.

The quality of water effluent from solvent extraction and adsorption is not well known. Probably solvent extraction is best for removing simple phenol (C_6H_5OH), less good for cresols and resinol, and least good for fatty acids and two ring phenols. Adsorption may be quite good for removing higher molecular weight phenols; the evidence is not conclusive.

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6. COOLING TOWER CONTROL

6.1 Introduction

Cooling towers in coal conversion plants have uncommon control problems because they will usually be fed with a mixture of source water and treated process condensate. Treated process condensate may have a lower salt content than the river water which decreases the possibility of scale formation by slightly soluble salts. On the other hand, condensate will usually have a higher organic content (phenol and COD) and a higher ammonia content than is common in cooling tower makeup. In this section we will estimate the consumption of cooling water and describe methods of dealing with the particular contaminants in the mixed feed.

One approach is to pretreat the process condensate to very low levels of ammonia and COD. Pretreatment techniques are the subject of most of this report so the cost of this approach can be, as it should be, estimated. If the process condensate is vigorously pretreated, then those cooling tower control problems unique to coal conversion disappear. In this case cooling tower control is no different from usual practice. Our purpose in this section is to show how a cooling tower might be controlled when the makeup water has organic contamination and to suggest upper limits to acceptable concentrations of contamination.

As found by most authors, it is useful to classify the problems of cooling tower control under four headings:

Scale formation

A wet cooling tower is an evaporator, and salts dissolved in the makeup water concentrate, often to the point of precipitation. The precipitate tends to adhere to heat transfer surfaces forming a hard scale.

Fouling

Not only may the makeup water contain silt and BOD which may be converted to sludge, but the circulating water in its passage through the tower scrubs dust out of the air. Circulating water thus contains an increasing amount of suspended matter, which will settle out in stagnant spots in the pipes and heat exchangers.

Corrosion

The well-oxygenated circulating water is very corrosive to heat transfer surfaces.

Biological Control

Circulating cooling water is warm and well-oxygenated and is an ideal habitat for microbial growth. The water is seldom sterile when fed to the system and, in any case, receives a steady supply of airborne growth. Untreated cooling systems are subject to fungal rot of the wooden parts of the tower, bacterial corrosion of iron and bacterial production of sulfide, algae growth in the sunlit portions of the tower, and suspended sloughed-off growth that can lodge in the system and block the flow. Biocidal chemicals must be added to control growth.

Before beginning the description of cooling tower control, the consumption of cooling water will be estimated.

6.2 Consumption of Cooling Water

To introduce the terminology of a cooling tower, the material balance can be written as

$$\text{Makeup} = \text{Blowdown} + \text{Evaporation}$$

By definition

$$\text{Cycles of Concentration} = (\text{Makeup})/(\text{Blowdown})$$

we also write

$$\text{Evaporation} = (\text{Cooling Load})/(\text{Heat dissipation rate}),$$ so

so

$$M(1 - 1/X) = Q_c/q \qquad (1)$$

where M = makeup rate, lb/hr

X = cycles of concentration

Q_c = cooling load, Btu/hr

q = heat dissipation rate, Btu/lb evaporated

The Cooling Load

This is the total rate of energy loss to the atmosphere through the cooling tower from the whole plant. If the plant is fully designed, the cooling load will be known. An accurate preliminary estimate can be obtained by considering the major points of cooling as described in References 1-4. If time for an estimate cannot be taken, we suggest assuming that the conversion plant is 65% efficient and that 25% of the unrecovered heat is dissipated by evaporative cooling. The cooling load will then be

(0.25)(1-0.65)(energy in total coal feed)

or

(energy in product fuel)(0.25)(0.35)/(0.65)

The Cycles of Concentration

This is decided upon in the usual way by comparing the cost of blowdown disposal with the cost of water treatment. When the cooling tower makeup is contaminated, blowdown to the river without treatment may not be suitable. In most coal conversion plants we foresee the need to limit the blowdown quantity so that it can be disposed of conveniently, for example, by using it to quench and wet the ash. This may eliminate blowdown treatment, but will usually require alternative treatment to permit high cycles of concentration without the formation of scale. We will return to the question of blowdown disposal in a later section.

Heat Dissipation Rate

In a cooling tower the air is heated at the same time as the water is cooled by evaporative and convective heat transfer. It is not correct to take the heat dissipation rate to be the latent heat of evaporation of water (1000 Btu/lb). A suitable estimating number is 1,400 Btu/lb evaporated. A sample of a rough estimate using the quantities discussed so far is given in Table 6-1.

A more accurate estimate of the heat dissipation rate requires climatic information. Given this information cooling tower calculations can be made month by month and the annual average heat dissipation rate determined. Cooling tower calculations are lengthy and the loss in accuracy will be less than 3% if the results of the calculations made by Leung and Moore[5,6] are used. Their results are shown on a copy of their graph as Figure 6-1. For any period of time, such as a month or a quarter of the year, for which the average wet bulb temperature and average relative humidity are known, the average heat dissipation rate can be read from Figure 6-1.

6.3 Scale Prevention

Scaling is prevented by controlling the concentration of species which form part of slightly soluble salts, particularly salts whose solubility decreases with an increase in temperature. These salts tend to precipitate

TABLE 6-1. APPROXIMATE MATERIAL AND ENERGY INFORMATION ON A 65% EFFICIENT COAL GASIFICATION PLANT

Product:	**10^6 Btu as gas**
Coal:	**$10^6/0.65 = 1.54 \times 10^6$ Btu** **Approximately 154 lb**
Unrecovered energy:	**0.54×10^6 Btu**
Fraction lost to cooling water:	**25%**
Evaporation rate:	**1400 Btu dissipated per pound of water evaporated** **96 lb water evaporated**
Coal ash:	**Approximately 15 lb**
Water lost with coal ash:	**35% moisture in wet solids** **8 lb water**
Concentration in cooling tower:	**13 fold**
Makeup:	**104 lb**

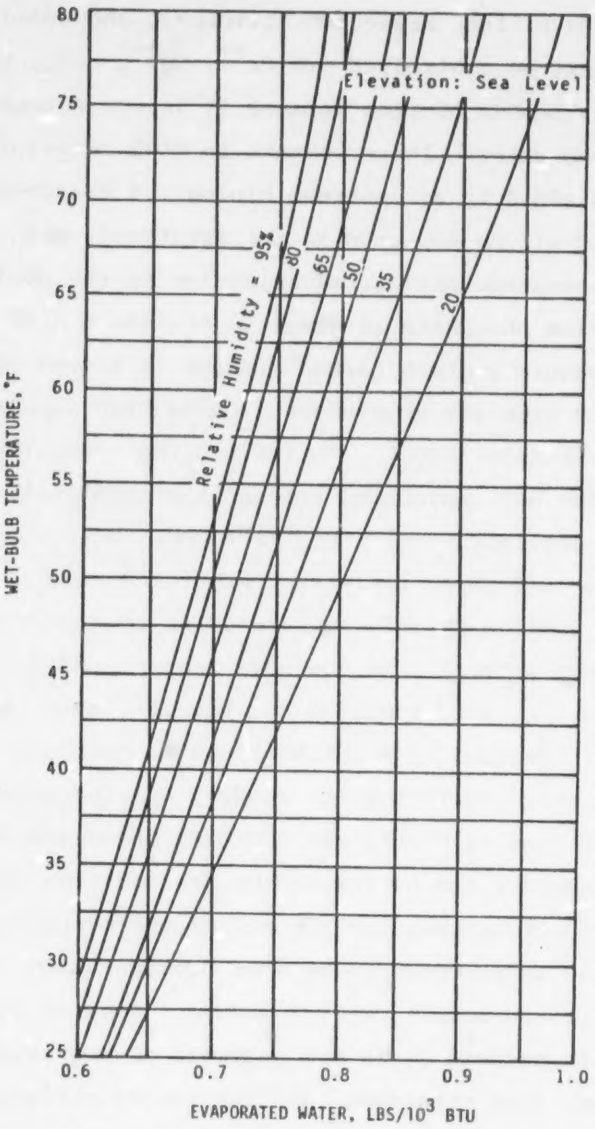

Figure 6-1. Pounds of water evaporated per 1000 Btu of heat transferred in a wet cooling tower.

on the surface of the heat exchanger forming hard, adherent scale. The most common scales are calcium carbonate and calcium sulfate with additional problems from silica, magnesium silicates, and calcium phosphates. The species that must be controlled are Ca^{++}, Mg^{++}, SiO_2, $CO_3^{=}$ and PO_4^{3-}. Phosphate deserves special mention because it is not a common component of cooling tower makeup water. It is present in coal conversions plants because (1) it was added to an upstream biological treatment plant as a nutrient and cannot all be consumed in the treatment, and (2) it is needed as a nutrient to encourage biological oxidation in the cooling towers. The solubility of calcium phosphate is given in Section 6.3.1.

Most makeup waters contain carbon dioxide in excess of the concentration in equilibrium with the atmosphere. Quite high alkalinities occur, nearly all as bicarbonate (HCO_3^-). In the cooling tower there is a tendency for CO_2 to be driven off converting some of the alkalinity to carbonate ($CO_3^{=}$) and causing precipitation. This is common and is usually prevented by adding sulfuric acid which replaces some of the alkalinity with equivalent sulfate. Scale by calcium sulfate is sometimes prevented by softening the makeup water. Lime and soda ash are added to precipitate calcium. This has the added advantage of removing some carbonate alkalinity as well. If desired, the softener can be operated to precipitate magnesium as hydroxide. Silica quite readily adsorbs onto the surface of magnesium hydroxide and is partly removed with the magnesium. This is advantageous. Phosphate can be removed by the addition of lime.

In addition to procedures for removal of the precipitating species, scale formation can be prevented even when precipitation is occurring by adding chemicals which inhibit crystal growth. Some of the most useful modern compounds to prevent scale are polymers of acrylates and acrylamide.

Acidification, lime treatment, and the use of antiscalants are not specific to coal conversion and are dealt with in other literature. Designs are not given in this report. The final point to be made is that no matter which treatment is used, dissolved salts will concentrate and some blowdown is essential to control their concentration in the circulating water. There is always some drift of water droplets from a cooling tower and this is a sort of accidental blowdown. When the circulating cooling water is very concentrated, the drift may damage foliage and land where it settles. For a high concentration cooling system, the best modern drift eliminators will be used. Blowdown cannot acceptably be prevented by allowing a high drift.

6.3.1 Solubility of Calcium Phosphate

Since phosphate is a contaminant not commonly found that will be found in most coal conversion plants, it is worth discussing its control. The solubility of calcium phosphate decreases as the pH increases. Calcium phosphate can be deliberately precipitated from a water stream by adding lime. Alternatively, precipitation can be prevented in circulating cooling water by lowering the pH. Solubility calculations suggest that the precipitation of calcium phosphate should be a serious problem. Experience suggests that it is not a problem[24]. A pseudosolubility product has been successfully used in water treatment[25] and the incorporation of this pseudosolubility product into a simplified solubility theory gives an equation which is probably adequate for determining the proper pH to prevent precipitation. This equation is derived below.

Simplified Theory

The least soluble salt is hydroxyapatite, $Ca_5(PO_4)_3OH$. Tricalcium phosphate, $Ca_3(PO_4)_2$, is also only very slightly soluble. If fluoride is present fluoroapatite, $Ca_5(PO)_3F$, which is the least soluble of all, may be found in the precipitate. Phosphate exists in solution in the forms H_3PO_4, $H_2PO_4^-$, $HPO_4^=$ and $PO_4^=$, in proportions dependent on pH. A method of determining permissible concentrations has been given by McCoy[15] for tricalcium phosphate. A much more complex procedure has been used by DeBoice and Thomas[25] who accounted for the presence of carbonate species plus twelve complexes. This complexity is not justified here because of the inaccuracies of the solubility products. McCoy used a graphical approximation which we have not thought to be necessary today when a calculator is readily available.

It is important to note, as stated by McCoy, that the following calculation predicts equilibrium values. With increasing alkalinity the rate of crystal growth is slowed and even at pH 8, several hours may elapse before any precipitation is formed. Furthermore, with suspending agents present the precipitate does not necessarily form a hard scale. Because of this the calculations have been approximated by making all activity coefficients equal to one.

Following McCoy[15] take

$$K_1 = 7.5 \times 10^{-3} = [H^+] \times [H_2PO_4^-]/[H_3PO_4] \qquad (2)$$

$$K_2 = 6.2 \times 10^{-8} = [H^+] \times [HPO_4^=]/[H_2PO_4^-] \qquad (3)$$

$$K_3 = 4.8 \times 10^{-13} = [H^+] \times [PO_4^{\equiv}]/[HPO_4^=] \qquad (4)$$

Analysis gives total orthophosphate which is

$$[o\text{-}PO_4] = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^=] + [PO_4^{\equiv}] \qquad (5)$$

To develop the required relationships we will need to express both $[PO_4^{\equiv}]$ and $[HPO_4^=]$ in terms of $[H^+]$ and $[o\text{-}PO_4]$ only.

From Equations (2), (3) and (4)

$$[HPO_4^=] = [H^+] \times [PO_4^{\equiv}]/K_3 \qquad (6)$$

$$[H_2PO_4^-] = [H^+]^2 \times [PO_4^{\equiv}]/K_2K_3 \qquad (7)$$

$$[H_3PO_4] = [H^+]^3 \times [PO_4^{\equiv}]/K_1K_2K_3 \qquad (8)$$

If Equations (6), (7) and (8) are substituted into Equation (5) and the equation is rearranged

$$[PO_4^{\equiv}] = [o\text{-}PO_4] \times K_1K_2K_3/F \qquad (9)$$

where

$$F = [H^+]^3 + K_1[H^+]^2 + K_1K_2[H^+] + K_1K_2K_3 \qquad (10)$$

$$= 10^{-3pH} + K_1 \times 10^{-2pH} + K_1K_2 \times 10^{-pH} + K_1K_2K_3 \qquad (11)$$

If the numerical values for K_1, K_2 and K_3, from Equations (2), (3) and (4), are put into Equation (10)

$$F = 10^{-3pH} + 7.5 \times 10^{-3-2pH} + 4.65 \times 10^{-10-pH} + 2.23 \times 10^{-22} \qquad (12)$$

Also, Equations (9) and (6) give

$$[HPO_4^{=}] = [o\text{-}PO_4] \times K_1K_2 \times [H^+]/F \qquad (13)$$

Equation (13) is used below to determine the solubility of hydroxyapatite.

Now consider the solubility of tricalcium phosphate. McCoy[15] gives

$$[Ca^{++}]^3 \times [PO_4^{\equiv}]^2 = K_{SCaP} = 5 \times 10^{-30} \qquad (14)$$

so,

$$1.5 \text{ Log } [Ca^{++}] + \text{Log } [PO_4^{\equiv}] = - 14.651 \qquad (15)$$

In Equation (15), $[PO_4^{\equiv}]$ can be taken from Equation (9) and numerical values can be substituted for K_1, K_2 and K_3 to obtain

$$1.5 \text{ Log } [Ca^{++}] + \text{Log } [o\text{-}PO_4] - \text{Log } F = 7.00 \qquad (16)$$

Finally, it is convenient to change the units of concentration. Let CaH (meaning calcium hardness) be the concentration of calcium in mg/l as calcium carbonate, then

$$10^5 [Ca^{++}] = CaH$$

Let $o\text{-}PO_4$ be total phosphate in mg/l, then

$$0.95 \times 10^5 [o\text{-}PO_4] = o\text{-}PO_4$$

In the new units Equation (16) becomes

$$1.5 \text{ Log CaH} + \text{Log } o\text{-}PO_4 - \text{Log } F = 19.478 \qquad (17)$$

Equation (17), with Equation (12), is an equation relating the concentration of calcium, the concentration of orthophosphate and the pH at equilibrium. If for any water the lefthand side of Equation (17) is greater than the righthand side, then the water is supersaturated. If the lefthand side is less than the righthand side, the water is undersaturated.

As an example, the permissible calcium hardness at equilibrium is given on Table 6-2 for various orthophosphate concentrations. The results for 10 mg/l are close to McCoy's results.

Now consider the solubility of hydroxyapatite. Truesdall and Jones[16] give the equation

$$Ca_5(PO_4)_3OH + 3H_2O \rightleftarrows 5Ca^{++} + 3HPO_4^{=} + 4OH$$

for which

$$\text{Log } K_{S.Ap} = 5 \text{ Log}[Ca^{++}] + 3 \text{ Log}[HPO_4^{=}] + 4 \text{ Log } K_w + 4 \text{ pH}$$

$$= -29.233 - \frac{8.996 \times 10^3}{T} \qquad (18)$$

For an example consider $K_{S.Ap}$ at 30°C when it has the value 1.19×10^{-59}. Take $K_w = 10^{-14}$. If $[HPO_4^{=}]$ from Equation (13) is substituted into Equation (16), if numerical values for K_1 and K_2 are taken, and if the units of concentration are changed as before, one obtains

$$1.667 \text{ Log CaH} + \text{Log o-}PO_4 - \text{Log F} + \text{pH}/3 = 21.670 \qquad (19)$$

Calculations from Equation (19) are also presented on Table 6-2. They are quite close to the results for tricalcium phosphate.

As a final example, Chen and others[17] in their tabulation use a solubility limit expressed as

$$(Ca^{++} \text{mg/l})^3 \times (\text{o-}PO_4 \text{mg/l})^2 = 0.06$$

or, in the units of this section,

$$(\text{CaH})^3 \times (\text{o-PO}_4)^2 = 0.94$$

If this is substituted for Equation (14) then Equation (17) becomes

$$1.5 \text{ Log CaH} + \text{Log o-PO}_4 - \text{Log F} = 19.137$$

which makes little difference. However, Chen and others use the solubility product at all pH which seems to limit all waters to the concentration permissible at a pH of about 10.

A More Practical Equation

In the circulating cooling water of many coal conversion plants we can expect about 10 mg/l phosphate and 600-800 mg/l calcium as $CaCO_3$. The solubility calculations given above suggest that a suspension of calcium phosphate will usually be present. Experience is that phosphate scale will not be troublesome, but most plants will require the addition of some suspending or antiscalant chemical.

For the purposes of water treatment, DeBoice and Thomas[25] have successfully used a pseudosolubility product

$$[\text{Ca}^{++}]^3 \times [\text{PO}_4^{\equiv}]^2 = 10^{-25.46} = 3.467 \times 10^{-26} \qquad (20)$$

This is very different from Equation (14). DeBoice and Thomas also used

$$K_1 = 7.2 \times 10^{-3}, \ K_2 = 6.3 \times 10^{-8} \text{ and } K_3 = 4.5 \times 10^{-13}$$

which are close enough to Equations (2) through (4).

If Equation (20) is used instead of Equation (14)

the righthand side of Equation (15) = -12.73

the righthand side of Equation (16) = 8.921

TABLE 6- 2. EQUILIBRIUM CONCENTRATIONS OF CALCIUM (in mg $CaCO_3$/l) FOR VARIOUS TOTAL ORTHOPHOSPHATE CALCULATED FROM EQUATIONS (17) AND (19)

		Equilibrium Calcium Concentration					
		for tricalcium phosphate			for hydroxyapatite		
orthophosphate (mg/l)		10	3	1	10	3	1
pH	Log F						
5.0	-12.122	1.73×10^4	3.85×10^4	8.02×10^4	1.34×10^4	2.76×10^4	5.34×10^4
6.0	-14.099	830	1850	3850	552	1140	2200
6.5	-15.045	194	434	902	119	244	472
7.0	-15.915	51	114	237	28	58	113
7.5	-16.653	16	37	76	8	17	32
8.0	-17.268	6	14	30	3	6	11
9.0	-18.325	1	3	6	0.4	0.8	1.6

TABLE 6-3. EQUILIBRIUM CONCENTRATIONS OF CALCIUM CALCULATED FROM EQUATION (21)

10 mg/l Orthophosphate

pH	Calcium as mg/l $CaCO_3$
5.0	330,000
6.0	16,000
6.5	3,000
7.0	980
7.5	310
8.0	120
9.0	24

and Equation (17) becomes

$$1.5 \text{ Log CaH} + \text{Log o} - PO_4 - \text{Log } F = 21.399 \qquad (21)$$

In Equation (21), F is given by Equation (12).

Calculations from Equation (21) are given in Table 6-3. Experience is lacking, but Equation (21) seems to give answers that are safe to use. Equation (21) is suggested for a control equation.

6.4 Biological Control

If treated wastewater is added to the cooling system, the control of biological growth can become a serious problem since the water contains nutrients. Relevant experience obtained in the petroleum industry has shown that, within limits, organic contamination is permissable in cooling water makeup.

In a cooling tower several changes occur in the circulating water. The first change is that ammonia is vaporized with water. Ammonia does not concentrate in a cooling tower and will be reduced in concentration if a large enough fraction (approximately more than 85%) of the makeup water is evaporated rather than blown down. This is easily calculated from vapor pressure data and has been demonstrated[7].

It has been completely demonstrated that refinery phenolic wastewaters can be used in a cooling tower and that bio-oxidation of phenol will occur with very high removal efficiencies. This has been practiced at the Sun Oil refinery in Toledo, Ohio[8], at the Mobil Oil refinery in East Chicago[9] and at other refineries according to a brief note by Maguire of Betz Laboratories[10]. In Table 6-4 we have tried to bring together some of the pertinent information.

It must be remembered that "phenol" in a refinery sour water probably contains a higher fraction of C_6H_5OH than will be found in the coal conversion wastewater, so the analogy is less than perfect. Mohler and Clere[8] identified several species of bacilli and cocci in their tower; five species utilized 200 ppm phenol and two of the five grew in a 1,000 ppm phenol/mineral salts medium. The bacteria were mesophilic with optimum growth in the range 60-100°F. Hart[9] reports that his towers operated at 80-86°F.

Necessary conditions for successful bio-oxidation are low sulfide[8] (below 2 ppm is suggested[10]), and only slow, small excursions in pH[8]. References 8 and 9 report a pH range of 7.8 to about 8.3. Hydrogen sulfide in coal conversion wastewater is lower than in stripped refinery sour water.

Chlorination to prevent slime was used at Mobil[9], but had to be carefully controlled to maintain bio-oxidation. Maguire[10] reports similarly and suggests the use of acrolein or other non-oxidizing biocides to prevent the formation of toxic chlorinated phenols. We recommend not using chlorine for coal conversion wastewaters because of the possible release of chlorinated aromatic compounds. Most of the suppliers of proprietary chemical mixtures can supply biocides other than chlorine. However, experience with these chemicals in a cooling tower which is intended to be biologically active has not been reported. We can make no firm recommendation.

Corrosion of steel has been low at both Mobil and Sun Oil. Low corrosion is also experienced when treated sewage is used in a cooling tower[11].

6.5 Suggested Limits on Quality of Makeup

Before setting quality limits of organic contamination in cooling system makeup, an example is useful. The Lurgi process plant designed by El Paso to make 250 x 10^6 scf/day pipeline gas in New Mexico will require cooling water makeup of about 1,500 x 10^3 lb/hr of which 50% will be treated process condensate. The quality of treated process condensate is not precisely known, but two estimates have been made[12,13]. They are reproduced in Tables 6-5 and 6-6. When treated condensate is diluted with an equal volume of San Juan River water, a probable composition of the mixture is that shown in Table 6-7. With the addition of acid and antiscale chemicals, this water can be concentrated eightfold and circulated at a pH of about 7.5 without scale formation[14]. It has been assumed by the designers, and we agree, that the organic contamination is not bad and that the tower will operate. The most important foreseeable problem is a high suspended solids as discussed below.

Of all the plant designs we have seen or made, the El Paso plant has the highest organic contamination in the makeup water. We have used this to suggest upper limits of permissable concentrations in makeup. The limits shown in Table 6-8 apply to the mixed makeup; they are high and will require good control by the operators, but they are not necessarily the maximum. Please recognize that the limits are rather arbitrary.

The limit on ammonia requires discussion.

Ammonia is driven off in a cooling tower and the most important limit to the permissable concentration in the makeup water is the formation of noxious fumes. Our calculations show that the odor threshold for ammonia in the cooling tower plume will not be exceeded with ammonia concentrations of up to

TABLE 6-4. EXPERIENCE WITH BIO-OXIDATION OF PHENOLIC REFINERY WASTEWATER IN A COOLING TOWER

	Sun Oil Refinery[8]	Mobil Oil Refinery[9]	Summary from Ref.10
Makeup concentration of phenol ppm	13 to 70	~ 14(a)	33 to 110
Fraction removed (%)	>99.4%	92-97% avg	> 90%
Tower loading:			
gpm/ft^2	3.3 to 3.4		
lb phenol/day	102 to 840	100	
lb phenol/(ft^3)(day)	~ 68(a)		

Notes:

(a) Estimate by us from information in the publication.

TABLE 6-5. CALCULATED EFFLUENT FROM PHENOSOLVAN PROCESS

(Reference 13)

	mg/l
Monohydric phenol	27
Polyhydric phenol	432
Other organics	1,834
BOD	2,151

Basis:

Assumed composition of crude phenol:
- 85% monohydric phenol
- 15% polyhydric phenol
- 5% other organics

Assumed extraction recoveries:
- 99.5% for monohydric phenols
- 60.0% for polyhydric phenols
- 15.0% for other organics

BOD_5 factors:
- monohydric phenols = 1.7
- polyhydric phenols = 1.9
- other organics = 0.7

TABLE 6-6. PHENOSOLVAN PLANT PERFORMANCE
SASOL FACILITY (From Ref. 12)
(For combined clean and contaminated gas liquor stream)

COMPONENT	INPUT Concentration, ppm
Phenols	3,250-4,000
Sodium	53
Ammonia (free)	10,600
Ammonia (fixed)	150-200
Suspended Tar & Oil	5,000
CN	6
Total S	228
Fatty Acids as $C_7H_4O_2$	600
CO_2	0.7%

COMPONENT	EFFLUENT Concentration, ppm
Phenols (Steam volatile)	1
Phenols (Bound)	60-160
Fatty Acids as $C_7H_4O_2$	560
Ammonia as Nitrogen	215
Hydrogen Sulfide	12
CN	1
Fluoride	56 gm/l
Chloride	25
Calcium (As Ca)	18
Iron (As Fe)	1 mg/l
Orthophosphate	2.5
Total Dissolved Solids	875
Suspended Solids	21
COD	1,126
pH	8.4

TABLE 6-7. PROBABLE COMPOSITION OF MAKEUP TO COOLING TOWER IN LURGI PLANT (50% from river & 50% treated effluent)

	mg/l
Phenols	100
BOD	1,000
COD	2,000
Ammonia as N	100
Total P	1
HCO_3	80
Ca	37
Mg	5
Na	22
Cl	17
SO_4	69

TABLE 6-8. SUGGESTED LIMITS ON MAKEUP TO A COOLING TOWER

	mg/l
Phenols	100
BOD	1,000
COD	>2,000
Ammonia as N	100
H_2S	2

500 mg/l so 100 mg/l (shown in Table 6-8) should be no problem. Because of ammonia, copper should not be used as a material of construction, and chlorination which is not planned will be reduced in efficacy.

6.6 Fouling Control

To prevent fouling by settled suspended solids in the circulating cooling water, it is necessary to keep the suspended solids below a concentration somewhere between 100 and 300 mg/l. When biological activity is going on, biomass can settle on and with other suspended solids and cause serious fouling. Thus, the lower limit on suspended solids is recommended.

Demonstrations with a refinery wastewater have shown[7] that about 50% of the organic carbon and most of the phenolics are removed in the cooling tower circuit. Thus, it is reasonable to expect that at least half of the BOD in the makeup will be oxidized in the cooling tower so that the sludge production rate will be about 0.2 lb sludge per lb BOD entering the system. Water having a BOD of 1,000 mg/l (as suggested in Table 6-8) has an equivalent sludge concentration of 200 mg/l and it is apparent that some form of solids separation is required. Of course the water shown in Table 6-8 has a high BOD. In many plants the BOD of process condensate will be reduced to about 50 mg/l by, for example, an activated sludge treatment. In these cases the sludge formed by bio-oxidation in the cooling tower, about 10 mg/l, is of little importance and the most important consideration is to ensure that water leaves the final clarifier of the bio-treatment plant with a low suspended solids, with filtering if necessary.

If the makeup does contain a high BOD resulting in the formation of a high concentration of sludge, the cooling tower basin must not be relied upon as a settling basin. Water is usually distributed over a cooling tower packing at more than 3 gpm/ft^2 and settling of biomass usually occurs at about 0.5 gpm/ft^2. The basin of a cooling tower is bigger than the packed area of the tower, but it is not that much bigger. Mohler and Clere[18] have found it worthwhile to skim the basin.

The recommended scheme is shown in Figure 6-2 and follows the concepts of Mohler and Clere[8,18]. They found that most of the BOD removal (about 90%) occurs in a cooling tower/cooling loop system very quickly, so concentrations of 1.1 cycles will suffice. They also found that 110 ppm suspended solids in the circulating cooling water had no adverse effects on heat transfer provided that the heat exchangers were backwashed systematically.

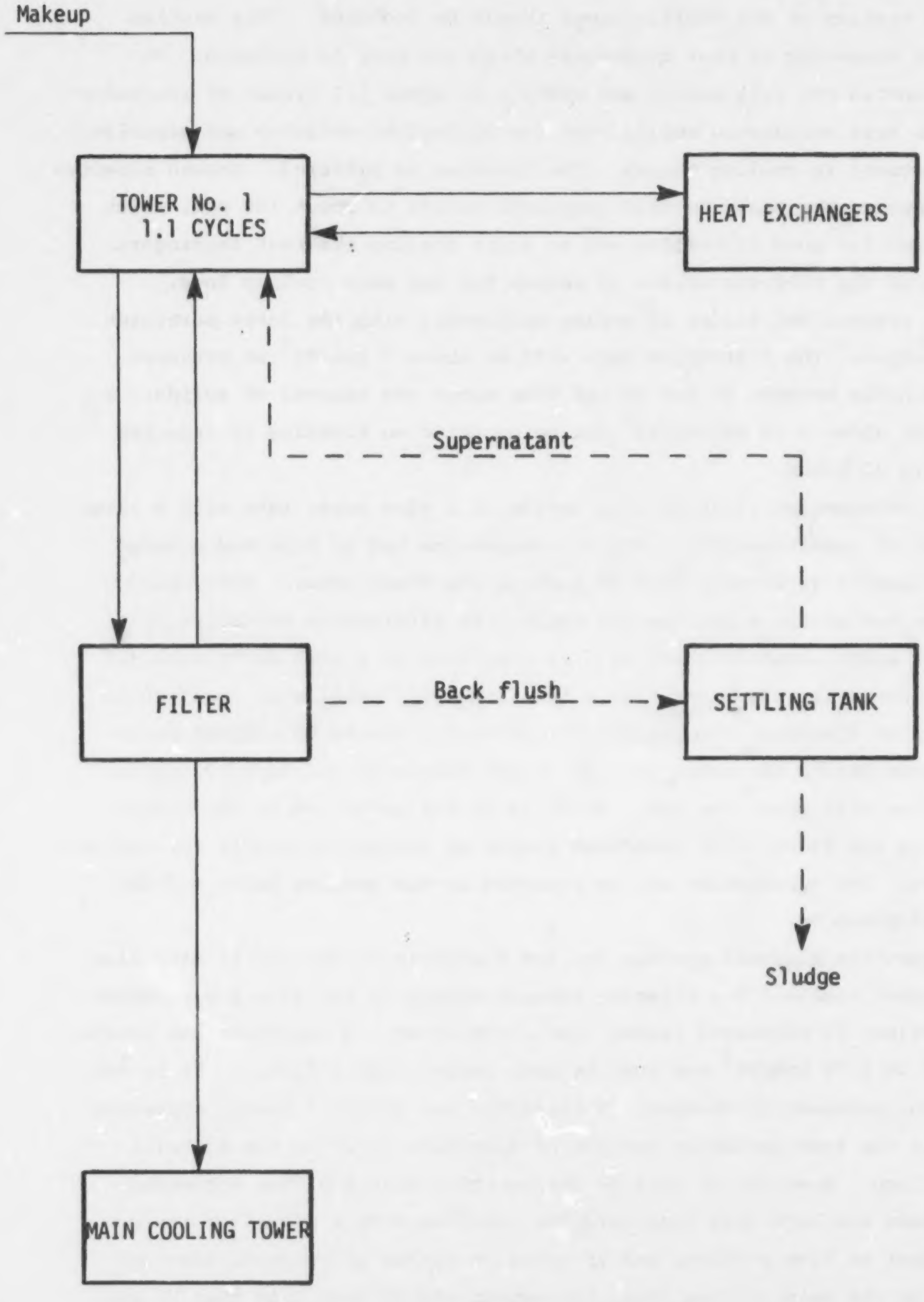
Makeup
TOWER No. 1
1.1 CYCLES
HEAT EXCHANGERS
Supernatant
FILTER
Back flush
SETTLING TANK
Sludge
MAIN COOLING TOWER

Figure 6-2. Control of solids from bio-oxidation in cooling loop.

One section of the cooling tower should be isolated. This section should be connected to heat exchangers which are easy to backwash. It should receive the full makeup and operate at about 1.1 cycles of concentration. The heat exchangers supply heat for biological activity and minimize the investment in cooling towers. The blowdown is filtered. Enough blowdown is returned to the basin to hold suspended solids to about 100 ppm, which is required for good filtration and to avoid fouling the heat exchangers. The rest of the filtrate serves as makeup for the main cooling loop.

The recommended filter is upflow multimedia with the large particles on the bottom. The filtration rate will be about 5 gpm/ft^2 at pressure drops probably between 15 and 60 psi with about 85% removal of solids. A loading of about 3 lb solids/ft^2 can be expected so flushing is required once every 12 hours.

The recommended flush is also upflow at a slow water rate with a large injection of compressed air. The air causes the bed to rise and a large space is needed to prevent loss of sand in the flush water. Free space above the bed should equal the bed depth. An alternative procedure is a short air-water scrub followed by 5 to 8 minutes of a high water rate (12 gpm); a second air scrub and fast water flush will usually be required to complete the cleaning. Compressed air injection should be stopped for a few minutes before the water rate is raised otherwise the rapidly rising air bubbles will upset the bed. About 4% of the water fed to the filter will be in the flush. The backflush should be allowed to settle for one or two hours. The supernatant can be returned to the cooling basin and the sludge disposed of.

A possible disposal process for the sludge is to dewater it with flue gas scrubber sludge. The filtrate becomes makeup to the flue gas scrubber.

A filter is suggested rather than a clarifier. A clarifier can handle only 0.5 to 0.75 gpm/ft^2 and must be much larger than a filter. It is not, therefore, necessarily cheaper. A clarifier can handle a higher suspended solids in the feed obviating recycle of clarified water to the number 1 cooling loop. However, it must be demonstrated that a higher suspended solids does not harm heat transfer. The overflow from a clarifier may not be as clear as from a filter and if about 10 cycles of concentration are planned in the main cooling loop, the makeup should have less than 20 ppm suspended solids. A clarifier will need flocculating chemicals. Mohler and Clere found a low usefulness for chemicals in their filter system.

6.7 Corrosion Control

The use of chromium or much zinc to control corrosion should be avoided. It is probable that nonmetallic corrosion preventing agents will be adequate. In most coal conversion plants the surface contacted by cooling water is not particularly hot, and it is on hot surfaces that nonmetallic corrosion inhibitors perform least well. Process streams are usually cooled to below 300°F in an air cooler; the water cooler follows the air cooler in series. Much of the cooling load may be condensers for steam turbines and here the temperature difference is not more than about 20°F. The hottest heat exchangers will be interstage coolers on gas compressors and here the use of corrosion resistant metals might be considered. Special metals will anyway be used for oxygen and hydrogen service and they might be considered for air compressors. Note that because of the presence of ammonia, copper alloys should not be used.

All the cooling towers should be operated just at the point where calcium carbonate precipitates. This allows a thin film of scale to protect the heat exchangers. Determination of the desirable pH involves tedious and lengthy calculations and some shortcuts have been given. Kunz, Yen and Hess[19] have measured the pH and the alkalinity in forty successfully operating cooling towers and find them related by the curve:

$$\text{pH} = 4.4 + 1.6 \text{ Log}_{10} \text{ (Alk)} \qquad (22)$$

with 90% confidence limits ± 0.75 pH units. In this equation alkalinity is expressed in mg/l as $CaCO_3$. Calgon Corporation supplies a slide rule for calculating the amount of acid to be added for desired cycles of concentration. The curve of Kunz and others is close to the curve recommended by Calgon.

There has been enough study on nonchromium corrosion control agents that a recommendation can be made.

Krisher[20] has conducted a series of tests and makes certain points. He successfully used polyphosphates and organic phosphonates. The tradeoff between more fouling and less corrosion is more prounounced than with chromate inhibitors and very careful control is needed. We recommend monitoring both scale formation (in one or two selected heat exchangers, or in a test section) and corrosion (by use of a meter), and adjusting the pH control regularly as needed.

Krisher points out that phosphorus is a nutrient but since our towers are intended to be biologically active, this is an advantage. Krisher suggests 50-100 ppm inhibitor, which will be expensive, but, as far as we can see, unavoidable.

Kumer and Fairfax[21] have tested several nonchromium corrosion inhibitors and rated them for anticorrosion effectiveness, scale formation and cost (1971 costs). They prefer an amino-phosphonate + polyacrylamide system.

Additional tests have been reported by Breske[22], whose two preferred nonmetal formulations were (1) a proprietary mix of phosphonate, polymer and copper inhibitor, and (2) a mixture of aminomethylene phosphonate, hydroxyethylidene diphosphonate, benzotriazole and hexametaphosphate. Benzotriazole is a copper inhibitor and may not be needed. Because of the presence of ammonia, copper should be avoided.

Vukasovich and Robitaille[23] studied the use of sodium molybdenate. Their best formulation was (mg/l in the circulating water), 5 mg/l Na_2MoO_4, 5 mg/l - hydroxyethylidene-1,1-diphosphonic acid, 5 mg/l 2-mercaptobenzothiazole, 2 mg/l $ZnSO_4$. The MBT is a copper inhibitor and, as mentioned, may not be needed.

There is enough agreement among the authors quoted that we suggest the following be tried for corrosion inhibition (mg/l in the circulating water; the suppliers mentioned are not necessarily the only suppliers)

hydroxyethylidene diphosphonate, 5 mg/l
(available from Monsanto)
sodium molybdate, 5 mg/l
(available from Climax)

If copper inhibition is required,

benzotriazole, 1 mg/l or mercaptobenzothiazole, 5 mg/l
(available from Sherwin Williams)

If inhibition is inadequate,

zinc sulfate, 2 mg/l or
sodium gluconate (Ref.23), 10 mg/l

In addition, an acrylamide-acrylate polymer will be added as antiscalant in an amount that differs for each plant.

6.8 Blowdown

Firm recommendations cannot be given for the disposal of cooling tower blowdown. The chosen method will depend on the local situation and regulations, the local source water quality, and on the coal conversion process and coal rank as these effect the quantity and quality of condensate fed to the cooling towers.

Blowdown will contain all the salts that were in the makeup. Traces of metals derived from coal and not natural to rivers may be present, but there is no information available. Probably the salts are natural to rivers and, depending on local preference, could be disposed of in the river, in the mine mixed with coal ash, or in a pond (lined or unlined). If concentration is required before disposal, evaporation using vapor compression evaporators will be used. If a concentrated waste is required, the cooling towers will be operated at the maximum safe concentration and the blowdown will be saturated. Concentration procedures intolerant of precipitation such as reverse osmosis, will, in the usual case, not be useful. Organic contamination may easily distill over during evaporation, decreasing the value of the distilled water. Dollar credit for this water, which is usually used as boiler feed, cannot be taken if an absorption cleanup step is required.

Blowdown will have some, but very little, contamination added to control corrosion and biofouling. This is controllable, and harmful or long-lived chemicals need not be used.

Blowdown will usually contain organic contaminants whose nature is unknown. We expect that these contaminants will have a high ratio of COD/BOD because most of the biodegradable material will have degraded. If concentration or destruction of the organic contamination is required, very general procedures should be considered until something is known about the nature of the the contaminants. Wet oxidation is the direct combustion of organic matter in water by air under pressure and it has a wide applicability. It is very expensive; the cost is proportional to the throughput and independent of the concentration so it should only be considered for highly contaminated waters where treatment is positively essential. Wet oxidation is described in

References 3 and 26. Adsorption, as described in this report, should also be considered if treatment is required. A suitable carbon or synthetic absorbent must be found. The recovered waste will probably be burnt. Adsorption has the advantage that the cost may not be strongly dependent on the effluent concentration so a clean water can be obtained.

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7. EQUIPMENT SIZING AND COSTING

7.1 Introduction

The equations for making preliminary size and cost estimates for the equipment required for the water treatment procedures described in the preceding sections are presented in this section in handbook style. The costing and sizing procedures described below are to be used to compare alternative water treatment schemes, and are not to be used for detailed design purposes.

7.2 Storage or Surge Vessels

The optimum length/diameter (L/D) ratio for a vessel of a given volume is dependent on the design pressure, the maximum allowable working stress of vessel shell material, the joint efficiency, and the corrosion allowance. For carbon steel vessels with design pressures under 200 psig, the savings realized by using L/D ratios greater than 2:1 are negligible. However, use of alloy steel shell materials at high design pressures strongly favors L/D ratios of 5:1 or greater if plot space permits.

7.2.1 Surge Vessels

The amount of liquid holding capacity required by a given surge vessel is usually determined by the amount of time required by the plant operator to intervene to prevent a serious upset in the downstream processing units. Liquid holdup times of 3 to 5 minutes are standard practice.

7.2.2 Reflux Drum

The volume required for a reflux drum is governed by both vapor and liquid handling capacity. In most circumstances the liquid handling capacity, described in Section 7.2.1, will dictate the vessel volume. For systems with partial condensers, the vapor handling capacity must be checked to determine if the cross-sectional area available for vapor flow is such that the vapor velocity (V) will not exceed:

$$V = 0.15 \left[\frac{D_l - D_v}{D_v} \right]^{0.5} \text{, ft/sec.} \qquad (1)$$

The available cross-sectional area is defined as the full cross-section for vertical vessels, or the transverse cross-section between the maximum liquid level and the top of the vessel for horizontal vessels.

7.3 Heat Exchanger Sizing

The required heat transfer surface area (A) is a function of the quantity of heat to be transferred (Q), the log-mean temperature difference (ΔT_{lm}) and the overall heat transfer coefficient (U_o). Equation 2 states the relationship between the above parameters:

$$A = \frac{Q \, \Delta T_{lm}}{U_o}, \text{ ft}^2 \qquad (2)$$

The heat transfer surface area can be estimated from using the following procedure: first, the heat duty (Q) and the log-mean temperature difference (ΔT_{lm}) are determined from the system mass and energy balances. Then, an overall heat transfer coefficient U_o is selected from tables such as those given in Reference 1. The estimated heat transfer area is then calculated from Equation (2).

7.4 Distillation Tower Sizing

The size of a distillation column is determined by the allowable vapor and liquid flow velocities, and the number of stages necessary to accomplish the required mass transfer. The column diameter is a function of the vapor and liquids loads. The vapor load for a given stage is defined as:

$$\text{V load} = \text{CFS} \left[D_v/(D_l - D_v) \right]^{0.5} \qquad (3)$$

where:

CFS = vapor rate, ft^3/sec
D_v = vapor density, lb/ft^3
D_l = liquid density, lb/ft^3

The liquid load is simply the liquid rate leaving stage n in gallons per minutes (GPM). Once the fapor and liquid loads have been determined, using methods described in previous sections of this manual, the column diameter can be estimated from Equation (4):

$$D = \left[V\ \text{load}\ (A + B \cdot GPM) + C \cdot GPM - D \right]^{0.5} \text{, ft} \qquad (4)$$

where:

	A	B	C	D
Tray towers	3.5	4×10^{-4}	3×10^{-2}	4.5
Packed towers	3.8	2×10^{-4}	7×10^{-3}	0.9

7.5 Cost Data

The cost data used in preparing the cost estimates in this manual are presented in this section in equation form:

$$\text{Cost} = k \times (\text{size parameter})^n\text{, \$} \qquad (5)$$

Table 7-1 lists the parameters for Equation (5).

After the major equipment cost has been determined, the total installed cost is estimated by multiplying the equipment cost by a Lang factor of 3.75 as shown below in Equation (6).

$$\text{Total installed cost} = 3.75\ (\text{major equipment cost})\text{, \$} \qquad (6)$$

TABLE 7-1. EQUIPMENT COST PARAMETERS

Equipment	Material	k	Size Parameter	n
Distillation towers	C.S	995	weight, lb	0.44
	SS	2786	weight, lb	0.44
Surge and storage vessels	C.S.	73	weight, lb	0.65
	SS	204	weight, lb	0.65
Heat exchangers, shell and tube	CS	44	area, ft^2	0.84
	SS	350	area, ft^2	0.69
Heat exchangers, reboilers	CS	292	area, ft^2	0.65

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